EVALUATION OF PHASE EQUILIBRIA FOR DILUTE MIXTURES FOR DESIGN PURPOSES

Geoffrey Ngigi, Diane Hildebrandt, David Glasser
Centre of Process and Materials Synthesis, School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Private Bag X3, WITS, 2050, South Africa. E-mails: geoffrey.ngigi@prme.wits.ac.za; diane.hildebrandt@comps.wits.ac.za; david.glasser@comps.wits.ac.za

Design of chemical processes almost always includes design for separation operations. Even though some novel separation processes such as membrane separation, pervaporation, and others, are now being implemented on the commercial scale, contact phase separation such as distillation, gas absorption, extraction remain the major separation processes. One of the essential ingredients for optimal design of such separation operations is knowledge of the required phase equilibrium. Vapor–liquid and liquid-liquid equilibria depend on the nature of the components, on their concentration in both phases, and on the temperature and pressure of the system. When dealing with non-ideal systems as is usually the case, obtaining phase equilibrium data experimentally requires appreciable experimental skill, experience and patient.

It is therefore an economic necessity to consider techniques for calculating phase equilibria for multicomponent mixtures from experimental data. Such techniques should require only a limited experimental effort and whenever possible should be based on a theoretical foundation to provide reliability for interpolation and extrapolation with respect to temperature, pressure, and composition to achieve a desired accuracy[1]. From a high purity separation unit design point of view, as one approaches infinite dilution regions, the value of activity coefficients become critically important in deciding the size of a separation unit. In this paper, we present a methodology that can be adopted in data evaluation where the relevant weight is given to available experimental data for a particular design objective.

KEYWORDS: phase equilibria, design, high purity separation

INTRODUCTION
In most industrial processes, the mixtures encountered usually have the properties of real mixtures and as such the deviation from ideality is normally described using fugacity (F) in the gas phase or activity coefficients (γ) in the liquid phase. At low pressures, the fugacity coefficient is usually obtained using the modified Raoult’s law and is very close to unity [1, 2, 3, 4, 5]. The activity coefficient (γ) is considered to be a function of only temperature and composition. The composition dependence models for excess Gibbs free energy are usually applied to determine the activity coefficients of liquid mixtures.

When one is designing for high purity separation process, activity coefficient (especially the limiting activity coefficients γ∞) becomes crucial. The limiting activity coefficient plays an important role and provides useful information for phase behavior
of dilute solution [5]. Such knowledge has been applied in many practical applications such as solvent selection, pharmaceutical analysis and environmental modeling. There are also used in extractive distillation, calculation of solid solubility in supercritical gases and in calculation of the critical micelle concentrations in surfactants.

The value of \( \gamma^\infty \) can be very large (thousands), especially for non-ideal systems, and the accuracy of predicting its value which is done using EOS in various mixtures is not adequate [1]. This means that prediction of vapor composition based solely on pure components boiling points can be grossly inaccurate, even for a simple flash drum. Activity coefficient models parameters are also dependent on temperature and thus extensive data may be needed to use these models for (multicomponent) mixtures over a range of temperature.

For liquid mixtures in which one or more of the components cannot be described easily by equations of state (EOS) in the liquid phase, e.g. mixtures containing alcohols, organic and inorganic acids, bases and electrolytes; excess Gibbs free energy models are used. Several modified Gibbs energy models (NRTL, Wilson, Uniquac, etc) or empirical correlation equations have been presented in open literature which in general considers molecular distribution in the first shell around the molecule while the rest is considered as a bulk solution [7]. For engineering application, especially in aqueous systems, an easy and generalized correlation method to evaluate \( \gamma^\infty \) with better accuracy is still required.

In this work, we look at how to model phase equilibria of dilute solutions. In particular we look at how we use the equilibrium data to model a separation process unit given high purity product specification and what factors are likely to influence the accuracy of the results in this very design intensive area.

**BACKGROUND TO THE INTERACTION BETWEEN THE DESIGN EQUATIONS AND VLE MODELS**

The product specification in some instances can be very demanding. For instance in the production of \( \alpha \)-olefins for co-monomer applications, it is necessary to produce a very pure final product. The purity specification of this product can be set as high as 0.9999. Achieving such high purity can be very demanding in size and operation of the separation process. A quick analysis of a distillation column designed for producing such high purity products shows the importance of obtaining accurate phase equilibria data especially near the pure component nodes and other pinch points. We begin by looking at the design equations for a distillation column.

**DESIGN EQUATIONS**

The differential mass balance for a rectifying section of a counter current distillation column (see Figure 1) is given by the equation [7–10] as:

\[
\frac{dx_i}{dn} = \frac{V}{L} (x_i - y_i) + \frac{D}{L} (x_{IP} - x_i) \quad \text{for all } i = 1, \ldots, m
\] (1)
Where $x_i$ is the mole fraction of component $i$ in the liquid; $y_i$ is the mole fraction of component $i$ in a vapor which is in equilibrium with the liquid of composition $x_i$; $x_iD$ is the mole fraction of component $i$ in the distillate, $m$ is the number of components in the mixture and $D$, $L$ and $V$ are distillate, liquid and vapor flow rates in the column respectively. The above equation assumes equimolar overflow and is accurate in difficult separations such as occurs in high purity separations.

Integrating equation (1) gives:

$$\int_{x_i,x_{in}}^{x_iD} \frac{dx_i}{(V/L(x_i - y_i)) + (D/L(x_iD - x_i))} = \text{ for all } i = 1, \ldots, m$$ (2)

Where $x_{i, in}$ is the composition of the liquid entering the rectifying section under consideration which has $n$ equivalent number of stages. It is important to realize that the above equation must be satisfied for each of the components in the $m$-component mixture. At the top of the column, $x_i \to x_iD$ and therefore the second term in the denominator of equation (2) in the integral tends to zero. Thus as we approach the high purity section in the column, equation (2) becomes:

$$\frac{L}{V} \int_{x_i,x_{in}}^{x_iD} dx_i = \frac{L}{V} \int_{x_i,x_{in}}^{x_iD} dx_i = n \quad \text{ for all } i = 1, \ldots, m$$ (3)

where $S_i = (x_i - y_i)$ of component $i$ of the separation vector, and is a function of composition $x$, temperature $T$ and Pressure $P$ of the mixture, and is given by:

$$S_i = (x_i - y_i) = x_i - \frac{x_i \gamma_i P_{i}^{vap}(T)}{\phi_i P} \quad \text{ for all } i = 1, \ldots, m$$ (4)

where $\gamma_i$ is the activity coefficient, $\phi_i$ is the fugacity coefficient and $P_{i}^{vap}$ is the vapor pressure of component $i$. We can see from equation (3) that it is important that we have
an accurate model of the separation vector, and that this becomes more and more important as the value of $S_i$ becomes smaller which occurs as the column profile approaches the high purity region where $x_i \rightarrow y_i$. We will now consider the various approaches that are currently used and their shortcomings. We will do this by considering an example, namely the separation of ethanol from water, at moderate pressures where $\phi \rightarrow 1$. For this purpose illustrating data analysis method discussed above, experimental data obtained from Dachema chemistry data series [4] (*Vapor liquid data collection*) was analyzed.

**ACTIVITY COEFFICIENTS AT INFINITE DILUTION**

At low pressure, for the dilute component, the separation vector for the dilute component becomes

$$S_i = x_i - y_i = x_i \left(1 - \frac{\gamma_i^{\infty}P_i^{vap}}{P}\right)$$

(5)

where $i$ is the dilute component in a binary mixture and $\gamma_i^{\infty}$ is the activity coefficient at infinite dilution. The values of the activity coefficient can be plotted as a function of composition at various total pressures for the water-ethanol system (Figure 2).

![Activity coefficient of ethanol vs. liquid mole fraction of ethanol in a water-ethanol mixture at different pressures (Data obtained from J. Gmehling, U. Onken Vapor liquid data collection Vol. 1, part 1 1977)](image_url)

**Figure 2.** Activity coefficient of ethanol vs. liquid mole fraction of ethanol in a water-ethanol mixture at different pressures (Data obtained from *J. Gmehling, U. Onken Vapor liquid data collection Vol. 1, part 1 1977*)
From Figure 2, we can see that as the ethanol concentration becomes dilute, the infinite dilution activity coefficient ($\gamma_i^\infty$) is a strong function of composition and pressure (and hence is sensitive to temperature). It will therefore not be particularly accurate to use equation (5) in the definition of the separation vector to estimate the column size using equation (3).

Henry’s Law Model
When dealing with such low contaminants concentrations (ppm levels), then Henry law is a convenient way of estimating a solute’s concentration. This implies that, to obtain the number of theoretical plates required in a rectifying column to shift a high purity $P_0$ to an even higher purity $P_n$, for instance, it is important to analyze data in the very top right end of the $y-x$ diagram [3]. In this region (dilute in $x_2$), the equilibrium curve is usually liberalized using the limiting slope (Henry’s constant) and the slope subsequently used in estimating the theoretical plates required.

Henry law states that the solubility of the solute in a solvent is directly proportional to the mole fraction of the solute in the gas phase [5]. In general the Henry’s law model becomes:

$$y_i = H_i x_i$$  \hspace{1cm} (6)

Thus if we plot the ratio ($y_i/x_i$) versus $x_i$ for the ethanol-water example, we would expect that in the dilute region the curve becomes a flat line. We see from Figure 3 that this does not in fact occur for ethanol in water, where ethanol is the dilute species.

Figure 3. Henry’s law constant for ethanol vs. mole fraction of ethanol for the ethanol-water system. (Data from J. Gmehling, U. Onken Vapor liquid data collection Vol. 1, part 1 1977.)
From this graph, it is observed that for this system, the Henrys Law coefficient for ethanol varies considerably with composition and temperature and therefore a Henrys law assumption will not give a good estimate of the composition in this region. Again this model will not give very accurate results for the value of the separation vector and hence will not be adequate for determining the size of equipment using the design equation (3).

We might consider Henrys law a first order model in that the mole fraction in the vapor phase is proportional to that in the liquid phase. We will now look at a higher order approximation that is proposed by the authors.

A SECOND ORDER APPROXIMATION: A CONSTANT JACOBIAN OF THE SEPARATION VECTOR
The separation vector in equation (4) is a function of composition only. Differentiating equation (4) with respect in composition (assuming $\phi_i = 1$) we obtain:

$$\frac{dS_i}{dx_i} = 1 - \frac{\gamma_i P_{i}^{\text{vap}}}{P} - x_i \left[ \frac{d\gamma_i P_{i}^{\text{vap}}}{dx_i} \right].$$

(7)

However, as opposed to other approaches discussed above, we now consider the component which is nearly pure. Then as $x_i \to 0$, we can see that $1 - \frac{\gamma_i P_{i}^{\text{vap}}}{P} \to 0$, and $P_{i}^{\text{vap}} \approx P$. Therefore equation (7) can be written as:

$$\left. \frac{dS_i}{dx_i} \right|_{x_i \to 1} \to - \frac{1}{P \frac{d}{dx_i} \left( \frac{\gamma_i P}{x_i} \right)} = - \frac{d}{dx_i} \left( \frac{y_i}{x_i} \right) \bigg|_{x_i \to 1}.$$  

(8)

This is a quadratic approximation as opposed to the Henrys law formulation, which is a first order approximation, and hence it might be expected to hold more generally and hence apply to more systems over a wider range of concentrations. Equation (8) predicts that if we plot $(y_i/x_i)$ versus $x_i$ for the concentrated component, the curve would asymptote to a straight line as $x_i \to 1$. The slope of this line is equal to the value of the Jacobian of the separation vector in a binary system. This term is also the same as the one that appears in the Jacobian of the separation vector in multicomponent systems for the component that is highly concentrated. In our opinion, this approach can be extended to multicomponent systems but because of the available space this can not be fully demonstrated in this paper.

We have plotted $(y_i/x_i)$ versus $x_i$ for both water and ethanol and this shown in Figures 4 and 5. It was interesting to note that curves for very different total pressures (0.1–6 atm), lie almost on top of each other over the whole composition range. At the azeotropes the ratio, $y_i/x_i = 1$, as expected and shown in Figures 4 and 5. We also see that the curves do in fact approach a limiting slope for both the concentrated ethanol and concentrated water cases. Furthermore the curves for different pressures, even though the temperatures are very different all approach the same limiting slope.
Figure 4. Plot of the ratio of mole fraction of water in the vapor to liquid phase vs. Mole fraction of water (Data from J. Gmehling, U. Onken Vapor liquid data collection Vol. 1, part 1 1977)

Figure 5. Plot of the ratio of mole fraction of ethanol in the vapour to liquid phase versus mole fraction of ethanol; (Data from J. Gmehling, U. Onken vapor liquid data collection Vol. 1, part 1 1977)
USE OF THE SECOND ORDER APPROXIMATION IN THE DESIGN EQUATION

We can rewrite Equation (3) as follows:

\[ n = \frac{V}{L} \int_{x_{i,\text{in}}}^{x_{i,D}} \frac{dx_i}{S_i} = \frac{V}{L} \int_{S_{i,\text{in}}}^{S_{i,D}} \left( \frac{dS_i}{S_i} \right) \left( \frac{dS_i}{S_i} \right) \]  

(9)

When one is designing for high purity \((x_1 \to 1)\), and letting \(\tau = V/L\), equation (9) becomes

\[ n \approx \tau \left( -\frac{d}{dx_i} \left( \frac{y_i}{x_i} \right) \right)_{x_i \to 1} \ln \left( \frac{S_{i,D}}{S_{i,\text{in}}} \right) \]  

(10)

where \(S_{i,\text{in}}\) and \(S_{i,D}\) are the separation vectors at initial and final composition stage in a column section respectively. The value of \(S_i\) can be calculated from:

\[ S_i = x_i(1 - x_i) \left( \frac{d}{dx_i} \left( \frac{y_i}{x_i} \right) \right)_{x_i \to 1} \]  

(11)

CONCLUSIONS

Achievement of high purity via distillation is extremely demanding on equipment size. To ensure reliable design calculations, engineers normally use conservative estimates which may be quite expensive from an economic and environmental point of view. Distillation column design, for example, relies heavily on the parameters used in the design models. It is shown from the simple analysis done in this work that the separation vector \((S_i)\) should be determined accurately as it relates to the size of the equipment. To achieve this, a good and dependable method of evaluating parameters is necessary especially when one is designing for high purity separations. Accordingly, the method(s) adopted must provide the correct asymptotes in the limits of compositions, and should also accurately predict the location of azeotrope. One has also to remember that even when we have experimental information available, there is always some risk when predictive methods are used, as it is possible that they do not provide enough accuracy for the process design parameters in the regions of interest.

It is also our suggestion that multicomponent systems can easily be treated as binaries. This suggestion is based on the understanding that as one approaches the limits of purity, the solute molecules are at infinitesimal concentration and each molecule is completely surrounded by the solvent molecules and vice versa. In such a limiting case, all solute molecule (different types) interactions with the solvent can be considered as parallel pairs of binaries. This is because the interaction of different solute molecules at
this low concentration is so small and can be ignored. The interaction parameters can therefore be calculated for each binary sequentially until the entire multi component system is described. It is from this basis that we propose that the method can easily be adopted for multicomponent systems.

REFERENCES