Advanced Engineering Separations

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Thomas Rodgers

UG Notes

Contents

List of Figures

List of Tables

Chapter 1

Ternary Diagram Manipulations

1.1 Tie-Line Correlations for Ternary Systems

In the case of many ternary systems with data gathered from literature only a few tie-lines have been experimentally determined. Direct interpolation of such data on triangular diagrams, and particularly extrapolation, ordinarily leads to inaccurate results, especially if there are very few tie-lines. Several methods of dealing with the problem have been devised.

1.1.1 Graphical Interpolation on Triangular Plots

One of the the key methods used for interpolation of tie-lines is on the triangular plots. To achieve this lines can be drawn from the equilibrium points constructing a line of intersection. For example, in Figure 1.1 taking the tie-line DE, we can draw a line from either end; a line DF which is parallel to axis BC and a line EF which is parallel to axis AC. The two constructed lines meet a point F. This process can be repeated for all the tie-lines. The resulting tie-line correlation curve PFG (or conjugation curve) is then produced by joining all these intercept points.

From any point on this curve, two lines constructed parallel to AC and BC will then intersect the solubility curve at concentrations corresponding to equilibrium tie-line pairs.

The curve PFG is not straight, although the curvature is generally quite small (except for near to the Plait point, P). The position of the Plait point can also be found using this method, via extrapolation, only when tie-lines very close to the Plait point are known.

Since the method in Figure 1.1 requires an extension of the plot below the base of the ternary diagram, it is not always convenient to draw. Therefore there is a modification available [5] which is very similar to Figure 1.1, but makes used of lines parallel to axis AB. This can be seen in Figure 1.2, where the points D, E, F, G are the same relative points. In this case the tie-line correlation curve PFG has much more curvature, therefore is somewhat less useful. This method can actually be performed with any pair of axis, it is just that some are more useful than other.

Hand (1961)[2] has presented an interesting method in plotting ternary data in such a manner as to make the tie-line parallel to the base of the triangular diagram, thus meaning that tie-lines can be easily interpolated and extrapolated as we know that they are all parallel. The Plait point is then at the maximum of the binodal equilibrium curve. This is achieved by scaling on of the coordinates, such that we operate in a new coordination system of,

$$\left(\frac{x_A}{x_A+Kx_B+x_C},\frac{Kx_B}{x_A+Kx_B+x_C},\frac{x_C}{x_A+Kx_B+x_C}\right) \tag{1.1.1}$$

where K is selected based on making,

$$\frac{x_A^1}{x_A^1+Kx_B^1+x_C^1}=\frac{x_A^2}{x_A^2+Kx_B^2+x_C^2} \tag{1.1.2}$$

for each tie-line. Figure 1.3 shows this method for the same system as Figure 1.1, where $K = 0.108$. It can be seen that many of the tie-lines are now parallel to the AB axis, but there is some variation. Although this method is very useful, it has not been investigated thoroughly to determine the extend of applicability.

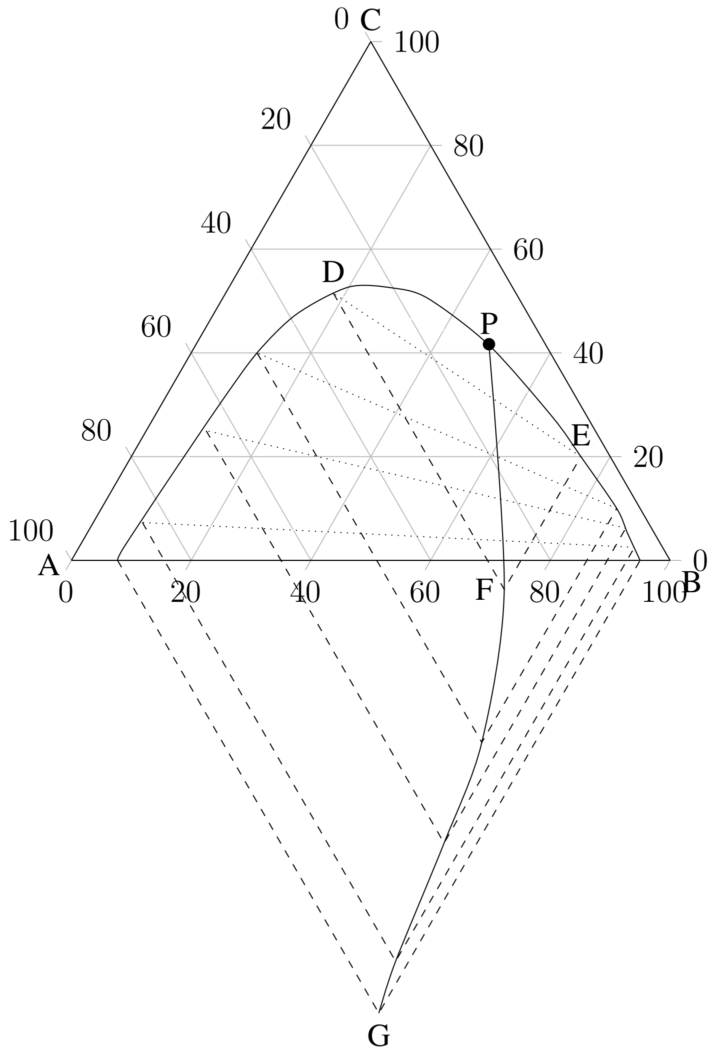


Figure 1.1: Graphical interpolation of tie-lines for an example system.

1.1.2 Distribution Curves

Many methods have been devised to plot the concentrations of the equilibrium solutions against each other to try to facilitate interpolation and extrapolation. These have advantages over the ternary diagrams as there are more transformations available, but have the disadvantage that often the ternary solubility curve is also needed in addition to these plots to get the full compositions.

The simplest distribution curve consists of a plot the concentrations of the solute C in the A-rich phase (x_{CA}) against the equilibrium concentrations of C in the B-rich phase (x_{CB}). Taking the ternary system given by Figure 1.4, then this plot can be given by Figure 1.5.

You will see that the points are above the 45° line, which means in this case that the component C prefers to be in the A-rich phase. As the Plait point is not on the maximum point of the binodal equilibrium curve, the distribution curve raises through a maximum and then drops to the Plait point. The ratio x_{CA}/x_{CB} at any point on the curve is called the distribution coefficient, and in the case of Figure 1.5 is approximated by the curve shown.

A second form that provides a curved distribution curve has also been proposed. This

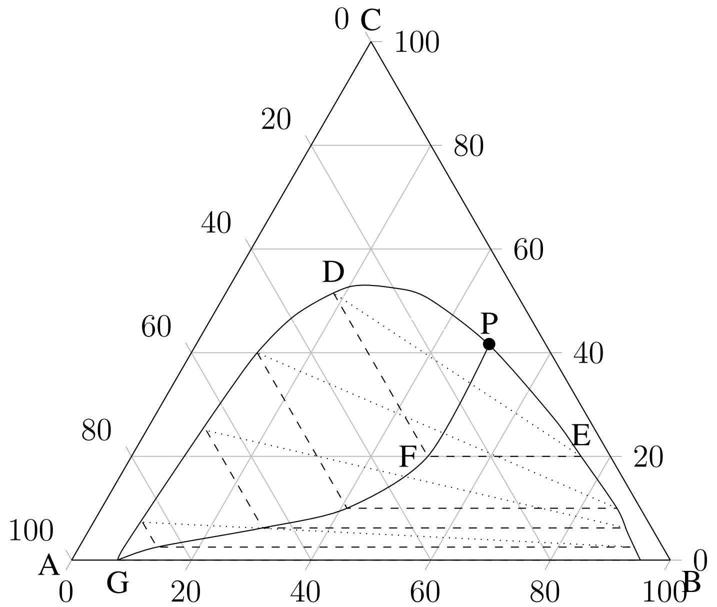


Figure 1.2: Sherwood graphical interpolation of tie-lines for the same example system as Figure 1.1.

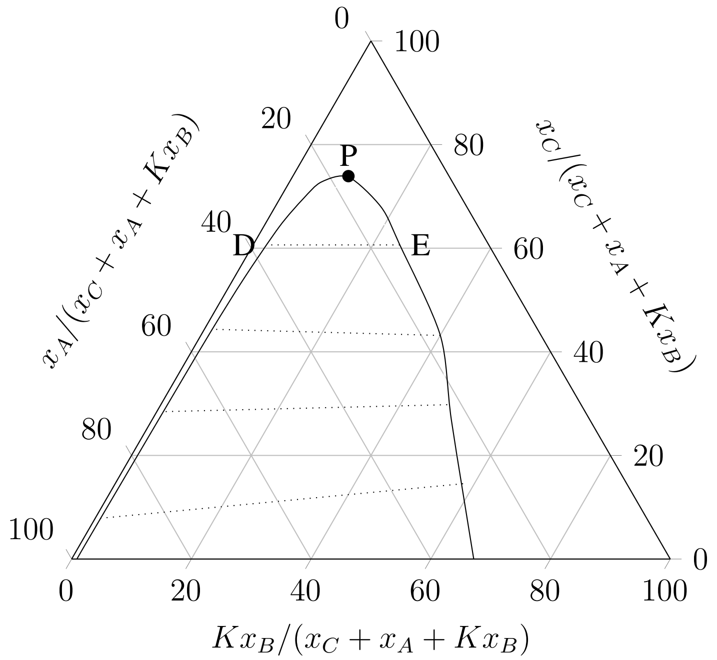


Figure 1.3: Hand graphical re-scaling of tie-lines for the same example system as Figure 1.1.

form, although works for type 1 systems, is especially effective for type 2 systems and produces plots very similar to vapour-liquid equilibrium plots [1]. This works by looking at the system on a B free basis, hence the coordinate system is,

$$\left(\frac{x_{CB}}{x_{CB} + x_{AB}}\right), \left(\frac{x_{CA}}{x_{CA} + x_{AA}}\right) \tag{1.1.3}$$

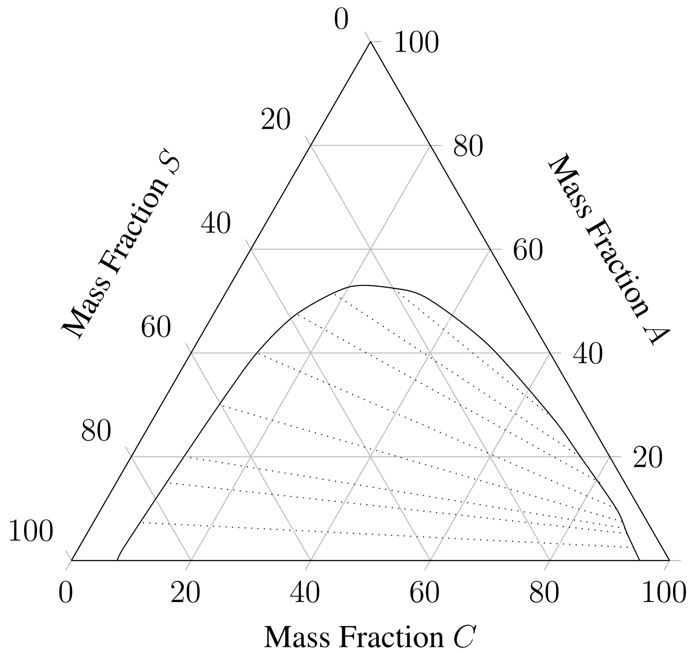


Figure 1.4: Ternary phase diagram for a general solute-carrier-solvent system.

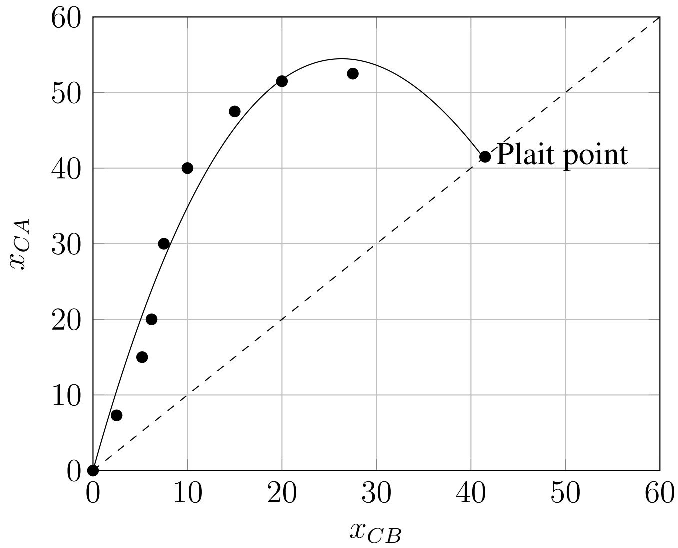


Figure 1.5: Distribution curve for C in the ternary system shown in Figure 1.4, with a best fit line shown for the data.

This data can then be fit with a constant relative volatility style equation,

$$\left(\frac{x_{CB}}{x_{CB}+x_{AB}}\right) = \frac{A\alpha\left(\dfrac{x_{CA}}{x_{CA}+x_{AA}}\right)}{A+(\alpha-1)\left(\dfrac{x_{CA}}{x_{CA}+x_{AA}}\right)} \tag{1.1.4}$$

where α is akin to a relative volatility and A is a constant based on the Plait point (for a type 2 system $A = 1$).

As well as these curved distribution curves, effort has been put into developing linear plots as these are easy systems to interpolate and extrapolate values. These systems rely on value transformation and log axis to achieve the straight lines. For many systems the

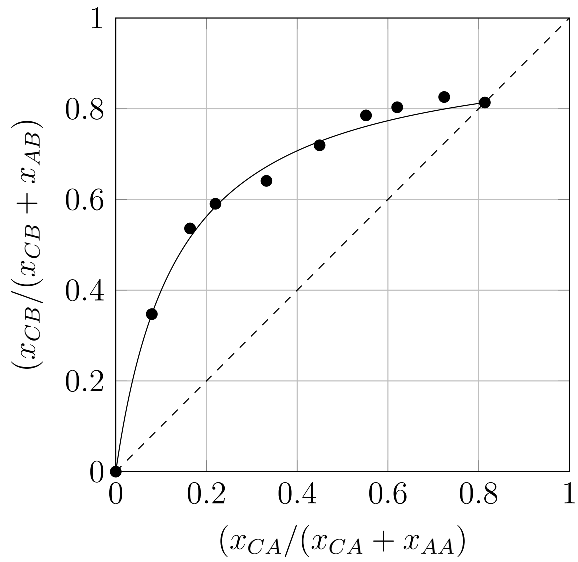
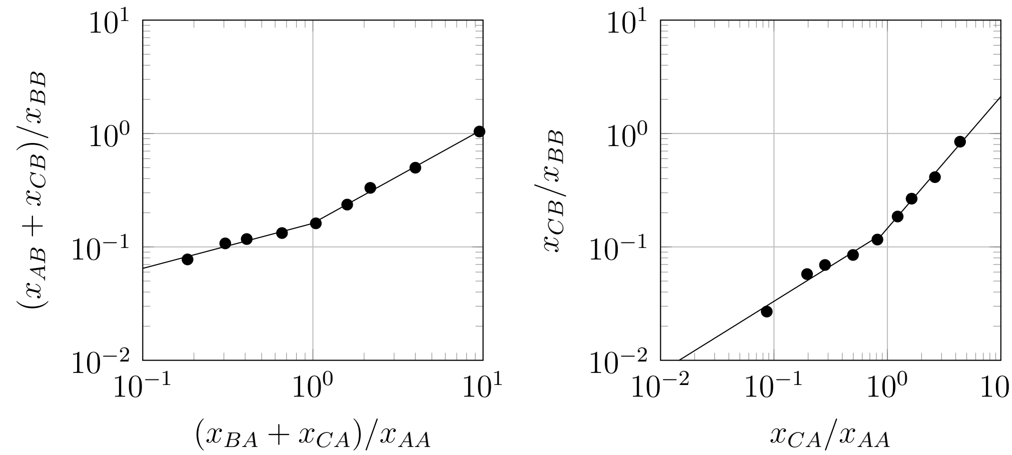


Figure 1.6: Vapour-liquid style distribution curve for C in the ternary system shown in Figure 1.4, with a best fit line shown for the data based on equation 1.1.4.

distribution curve can be represented as either 1 or 2 straight lines. Figure 1.7 shows two example transformations. The advantage of these plots it that if you are confident that the system is represented by a single straight line then very few tie-lines are needed to allow calculations for the system.



(a) Othmer-Tobias coordinates [4]

(b) Hand coordinates [2]

Figure 1.7: Linear distribution curve examples for C in the ternary system shown in Figure 1.4.

1.1.3 Prediction of the Plait Point

Several of the methods previously discussed have the ability to predict the position of the Plait point but only if tie-lines are known close to the Plait point. Therefore if we need to know the position of the Plait point it is useful to have a repeatable method. The Plait point mixture has a critical temperature and pressure equal to the conditions for which the diagram is plotted, so is a key point for the diagram.

Treybal (1946) [7] extends the Hand plot [2] to include the binodal equilibrium curve plotted as x_c/x_B against x_C/x_A on the same axis. At the Plait point the distribution line meets the equilibrium curve, as shown in Figure 1.8.

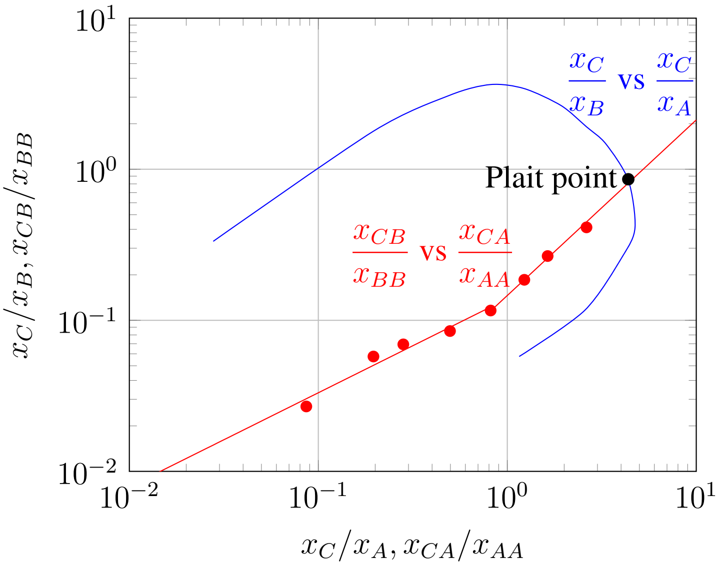


Figure 1.8: Linear distribution curve for calculation of the Plait point for the ternary system shown in Figure 1.4.

1.2 Rectilinear Representations of Ternary Diagrams

For some purposes,a plot of the ternary equilibrium dataon rectangular coordinates is preferable to triangular plots. Several of these methods have been developed, but potentially the most useful is where the coordinates are represented as,

$$\left(\frac{x_C}{x_A + x_C}\right), \left(\frac{x_B}{x_A + x_C}\right) \tag{1.2.1}$$

as shown in Figure 1.9 [3]. An alternative option is given by Figure 1.10 [6] which keeps the direction of the binodal equilibrium curve using the coordinate system,

$$(x_c + 2x_B)\sqrt{3}, (x_C) \tag{1.2.2}$$

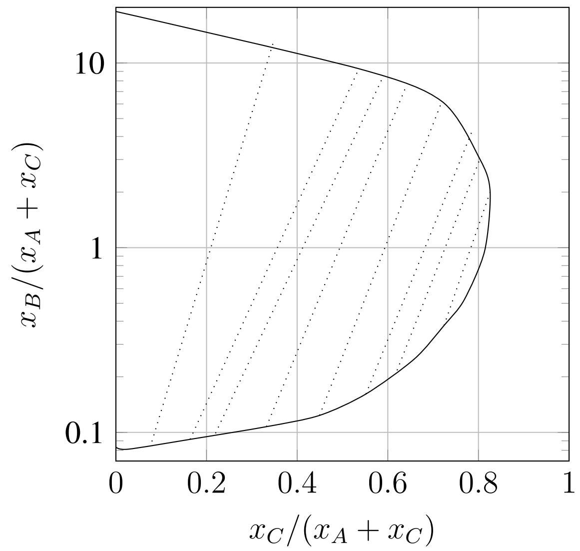


Figure 1.9: Rectilinear representation of the ternary system shown in Figure 1.4.

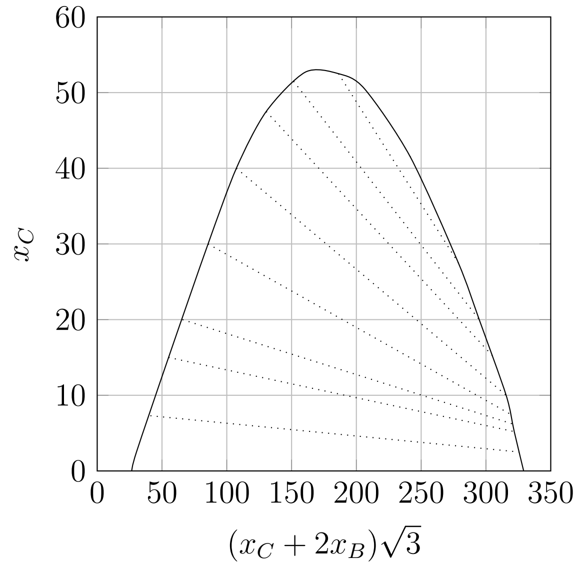


Figure 1.10: Alternative rectilinear representation of the ternary system shown in Figure 1.4.

1.3 References

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