EFFECT OF THE PLAINT POINT POSITION ON THE SHAPE OF SPINODAL CURVE DETERMINED BY WHEELER-WIDOM MODEL

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Very recently the spinodal curves of some water(1)–1-alkanol(2)–1-propanol (3) systems that present a Type I solubility gap (1-alkanol = 1-butanol, 1-pentanol, 1-hexanol) have been calculated by using the Generalized Wheeler-Widom-Huckaby model with a local fitting procedure which requires, as input data, the experimental coordinates of the plait point. Because the experimental plait point position can be affected by a significant error, we tested in this paper the effect of changing artfully the location of the plait point on the final position of the spinodal curve.

\textit{Key words}: Ternary system, amphiphilic solvent, Wheeler-Widom model, spinodal curve.

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\section{1. INTRODUCTION}

In the last year some of us have published the results of a new and efficient calculus procedure that permits to obtain the spinodal curve of the system, starting from the Liquid-Liquid-Equilibrium (LLE) data of a ternary system and applying the Generalized Wheeler-Widom-Huckaby Model (GWWHM) in the Mean Field Approximation (MFA) \cite{1–3}. In this procedure it is central the knowledge of the composition of the plait point (PP) of the system. By the experimental point of view the plait point composition is the result of a complex procedure and therefore could be affected by a significant error. To analyze as the uncertainty on the PP composition can influence the position of the spinodal curve, we have determined, for a test system, the binodal points by using the experimental PP composition \((x_{PP}^{exp}, y_{PP}^{exp})\) and then some other fictitious compositions for the plait point \((x_{PP}^{∗}, y_{PP}^{∗})\); these compositions were chosen as \(x_{PP}^{∗} = x_{PP}^{exp} \pm K \cdot \Delta x_{PP}\) with \(K = 1, 2\) and where \(\Delta x_{PP}\) is a suitable value (for \(y_{PP}^{∗}\) is valid the relation \(y_{PP}^{∗} = f(x_{PP}^{∗})\) where \(f(x)\) is the polynomial that represents the experimental binodal curve). The composition of a ternary system can be specified by two parameters that are generally chosen as the mole fraction of two components, \(e.g.\ X_1\) and \(X_2\). In this paper we will instead use the Cartesian coordinates \(x = (X_1 - X_2) / \sqrt{3}\) and \(y = X_3\). In the following we will report: 1) a condensed
description of the Generalized Wheeler-Widom-Huckaby Model (GWWHM) and of the procedure recently published to obtain the spinodal curve, 2) a short explanation of the procedures used to obtain the plait point composition, 3) a description of the results obtained in the simulation performed with different PP compositions and 4) a discussion of these results.

2. GENERALIZED WHEELER-WIDOM-HUCKABY MODEL (GWWHM) AND THE PLAIT POINT LOCAL FITTING METHOD (PPLFM)

The GWWH model is the actual evolution of the original Wheeler-Widom Model (WWM) [4] that considered a ternary system presenting a solubility gap of Type I as constituted by two solute molecules \( AA \) and \( BB \) and an amphiphilic solvent molecule \( AB \). The molecules were supposed to cover completely the bond, one per bond, of a regular lattice; the cross-interactions, \(-A\cdots B-\), were forbidden while the self-interactions, \(-A\cdots A-\) and \(-B\cdots B-\), were supposed to have the same energy. The above conditions allow a direct analogy of WWM with the Ising model [5] defined on the same lattice. The model corresponds to a ternary system with completely insoluble solutes, with a symmetric binodal curve (BC), with tie-lines (TL) parallel to the solute composition axis and with no effect of the temperature. The actual upgraded model, GWWHM [6–12], accounts for the presence of two- and three-body interactions between the molecular ends, and permits to describe systems with non-zero solubility between the solutes, with asymmetrical BC, with tie-lines with slopes different form zero and with temperature effect on the coexistence curve. The actual model is equivalent to the standard Ising model on a 3-12 lattice and if solved exactly can return the BC while if solved in the MFA can give the spinodal curve SC; if the interest is in the SC also the BC is calculated, for internal consistency, in MFA. The main feature of GWWHM is the possibility to describe the binodal and the spinodal curves with two different equations using the same composition parameter \( M \) and the same two constant parameters \( \tau \) and \( \Delta \). Then the calculus of the spinodal curve could seem very straightforward: the GWWH binodal equation can be fitted to the experimental LLE data to evaluate the fitting quantities \( M, \tau, \) and \( \Delta \) that can then be used to compute the spinodal curve. Unfortunately even for systems with almost symmetric solubility gap, the fitting of the LLE data with a single theoretical binodal equation is not accurate enough. It happens that only some portions of data are well interpolated by the GWWH binodal equation while for other portions the fitting is quite poor. In order to overcome this problem we have proposed a local fitting procedure described in details in the previous papers [13]; this procedure allows for any select point of the binodal curve to calculate the corresponding spinodal point and then, at the end of the procedure, the final spinodal curve for interpolation of the spinodal single points. Because for each binodal composition
the GWWH binodal equation requires three parameters, the composition parameter $M$, and the constants $\tau$ and $\Delta$, it is necessary to write a system of three equations that characterizes the binodal theoretical equation relative to the chosen point. The choice of the first two equations is trivial because it is obvious to impose that the theoretical binodal curve has to pass through the selected binodal point while the choice of the third equation is free. We have explored three different possibilities for this last equation and developed three different calculation procedures [1, 14, 15]. The first two work very well with almost symmetrical coexistence curves but fail with the asymmetric ones. The third gives good results even for asymmetrical binodal curve with a plait point far from the maximum of the curve. In this procedure, Plait Point Local Fitting Method (PPLFM), the third equation imposes that the distance between the theoretical plait point of each selected binodal point and the experimental plait point must be as small as possible [1].

3. THE EXPERIMENTAL PLAIT POINT

The LLE data reported in literature can be distinguished in: i) single binodal points, and ii) couples of binodal points in chemical equilibrium (the straight line joining each couple of conjugate solutions is indicated as tie line). The plait point of a coexistence curve can not be experimentally determined but can be obtained only by using the compositions of the conjugate solutions and some semi-empirical extrapolation procedures. In principle the knowledge of the conjugate compositions is not necessary for the calculation procedure reported here but we will discuss their determination and precision because they are involved in the Plait Point estimation [16–18]. The composition of a single binodal point can be determined by a single step titration method [16–19]. To a known amount of a binary heterogeneous mixture of the two solutes, at known composition, the solvent is added drop to drop until the opalescence disappears; this point is the binodal point we were seeking and its composition can be easily calculated knowing the amount of the three components. These measurements are quite rapid, do not require sophisticated equipment, except a good thermostatic bath; because the passage from an opalescent solution to a limpid one, that represent the end point of the titration, is easy to appreciate the errors are usually small as the typical errors of a volumetric titration [19]. A set of binodal point compositions allows drawing the binodal curve but it is not sufficient to obtain the activity parameters of the system. For this purpose the knowledge of conjugate solutions is mandatory. The determination of the compositions of two conjugated solutions, i.e. two solutions in chemical equilibrium, is more elaborated [16]. A ternary heterogeneous mixture with a composition under the binodal curve is stirred for a suitable period, a few hours depending on the fluidity of the system, and then allowed to separate in the two solutions in chemical equilibrium; the time of separation is variable.
between few hours to 1 or 2 days. The subsequent step is to take carefully apart samples of the two separated phases and determine their analytic compositions; this can be done or by comparing the values of two or more physical and chemical properties of these solutions with the values of the same properties for solutions at known composition, or by direct determination of the amount of at least two components of the solution. According to the first procedure it is necessary the use of calibration curves. Very often the measurements of the calibration curves can not be performed close to the binodal curve and then this procedure often requires to dilute the conjugate solution to reach the concentration range of validity of the calibration. The second procedure is at the moment the most used. The techniques employed for the direct quantitative determination of at least two components in solutions depend on the nature of the components themselves; acid-base titration, gas-chromatography, H nuclear magnetic resonance, and several different spectroscopies are the most used. In some of these techniques calibration curves are also needed. The compositions of the conjugated solutions are systematically affected by a larger error than the single binodal compositions. The equilibration, the separation of the two phases, and the levy of pure samples of the two separated solutions are delicate processes that can lead to large uncertainty in the final results. To these errors, those due to the eventual dilution of the conjugated solutions, those in the calibration curves determination, and those typical of the used physical – chemical properties must be added. For this reason, very often, the conjugated compositions do not lie, as would be expected, on the binodal curve obtained by interpolation of the experimental binodal points. For this reason the researcher have tried in the past to test the reliability of a set of conjugated compositions by using some semi-empirical equations. These equations are inspired to the Nerst distribution law [20]: it assumes that the distribution coefficient of a species that is dissolved in two phases in thermodynamic equilibrium is a constant no matter the composition of the two phases. Considering the two unmiscible species as components 1 and 2 and the solute as component 3 and the two phases $A$, rich in component 1, and $B$, rich in component 2, this should imply:

$$K_3 = \frac{(a_3)_A}{(a_3)_B} = \frac{(X_3 \gamma_3)_A}{(X_3 \gamma_3)_B}$$

(1)

where $(\gamma_3)_A$ and $(\gamma_3)_B$ represent the activity coefficients of the component 3 in both the phases $A$ and $B$. The distribution can empirically be described in term of the Hand equation [21]:

$$\frac{(X_3)_A}{(X_1)_A} = k \left[ \frac{(X_3)_B}{(X_2)_B} \right]^n$$

(2)

where $k$ and $n$ are adjustable parameters. This equation as those of Othmer – Tobias [22], equation (3), and Bachmann [23], equations (4) and (5), have been extensively
used to correlate the experimental tie lines:

\[
\ln \left[ \frac{1 - (X_1)_A}{(X_1)_A} \right] = m + p \ln \left[ \frac{1 - (X_2)_B}{(X_2)_B} \right],
\]

\[(X_1)_A \cdot (X_2)_B = a \cdot (X_1)_A + b \cdot (X_2)_B,
\]

\[
\frac{(X_2)_B}{(X_1)_A} = -\frac{a}{b} + \frac{1}{b} (X_2)_B,
\]

where \(m\), \(p\), \(a\), and \(b\) are adjustable parameters. The validity of these empirical equations was investigated carefully by Carniti et al. [24]; they came to the conclusion that these equations can never be used to check the correctness of the experimental data. Nevertheless, even after this analysis, many authors have used these equations to check the experimental data and to obtain the plait point composition.

The way to obtain the plait point composition using the above equations is conceptually straightforward; determined the fitting parameters of the chosen equation by using the experimental tie line end compositions, the PP composition is obtained considering that in this point the compositions of the two solutions in thermodynamic equilibrium are coincident. The reliability of \((x_{exp}^{PP}, y_{exp}^{PP})\) is then strictly correlated to the validity of the previous equations strongly criticized by Carniti et al. (it is to observe that no one of the methods that use equations (1) - (5) for determining the plait point composition is reported in reference [16] that can be considered one of the best textbook on the liquid - liquid equilibria).

If the previous equations are not used to evaluate the plait point compositions it is obvious that the \((x_{exp}^{PP}, y_{exp}^{PP})\) coordinates must be determined by an extrapolation procedure by using the characteristic of the experimental tie lines. Coolidge suggests a graphical method [25, 26]. Two conjugated compositions are connected by the tie line and by using this segment as a basis two opposite triangles are constructed with the other sides parallel to those of the concentration diagram. This construction is repeated for each couple of conjugate compositions i.e. for each tie – line; the curve interpolating the vertices of these triangles outside the tie – line intercepts the binodal in the plait point (ref. 16 p. 278). A much more complicated procedure is reported in a more recent paper [27] where the authors employed a non-classical description of the behavior in the vicinity of the critical point; the procedure has given good results in some cases. It is evident that, independently by the methods used to obtain it, the error on the composition of the plait point is not negligible. Then the uncertainty of the plait point position requires a systematic study to verify its effect on the spinodal curve determined by the Plait Point Local Fitting Method (PPLFM); we have performed this analysis by using the LLE data of the system water – 1-pentanol – 1-propanol present in literature.
4. CALCULATION PROCEDURE

For the system water (1) – 1-pentanol (2) – 1-propanol (3) we have used in our analysis the following literature data at 25°C:

- 43 binodal points and the plate point [28–30],
- 1 couple of conjugated points for the binary system water (1) – 1-pentanol (2) [31].

We remind that for the PPLFM we do not need the compositions of the conjugated solutions and then we have not reported the 17 compositions of the tie line ends present in the literature. In the Cartesian coordinates, the (43 + 2) binodal points have been fitted to a polynomial of 4th order obtaining the Representative Experimental Binodal (REB) indicated as $y = f_{REB}(x)$ characterized by the following values of the coefficients:

- $a_0 = 0.699894$ ,
- $a_1 = -0.765257$ ,
- $a_2 = -1.222163$ ,
- $a_3 = 1.559177$ ,
- $a_4 = 0.800492$ .

As noted instead than note in paper [1], the experimental plait point, as determined with the Coolidge graphical method [28], (0.4598, 0.1691) does not lie on the interpolated polynomial; this is not uncommon for the reasons analyzed above. In these cases we preferred to use the so called Representative Experimental Plait Point (REPP) obtained as the normal projection of the experimental plait point on the REB. The abscissa of this point results $x_{RPP} = 0.4527$; the correspondent ordinate $y_{RPP}$ results from the REB equation: $y_{RPP} = f_{REB}(x_{RPP})$. For simplicity from now on we will indicate the coordinates $(0.4527, f_{REB}(0.4527))$ as $(x_P, y_P)$. The coordinates of the plait points used in this analysis will be indicated as $(x_P^{(±K)}, y_P^{(±K)})$ where $x_P^{(±K)} = x_P^0 ± K \cdot \Delta x_P$ and $y_P^{(±K)} = f(x_P^{(±K)})$ with $K = 0, 1, 2$ and $\Delta x_P = 0.01$. The following plait points are then considered in this simulation analysis:

\[
\begin{align*}
(x_P^{(-2)}, y_P^{(-2)}) &= (-0.4727, 0.1337843) & \text{Fig. 1 orange point,} \\
(x_P^{(-1)}, y_P^{(-1)}) &= (-0.4627, 0.144522) & \text{Fig. 1 green point,} \\
(x_P^{(0)}, y_P^{(0)}) &= (-0.4527, 0.154789) & \text{Fig. 1 black point,} \\
(x_P^{(+1)}, y_P^{(+1)}) &= (-0.4427, 0.164584) & \text{Fig. 1 blue point,} \\
(x_P^{(+2)}, y_P^{(+2)}) &= (-0.4327, 0.173909) & \text{Fig. 1 red point.}
\end{align*}
\]
These values are reported in Figure 1 with the representative experimental binodal. It is worth noting that the displacement $\Delta x_P = 0.01$ used to fix the compositions of the fictitious plait points is almost of same order of magnitude of the difference $|x_{PP} - x_{RPP}|$. The analysis will give then reasonable indication of the effect that real error of the plait point composition will give using our procedure to obtain the spinodal curve. Obtained the REB polynomial, the PPLFM is applied to some selected points of this curve. These points indicated as fitting points have been chosen as it follows:

- For the left branch of the binodal, i.e. for the compositions in the range between the water rich binary phase composition and that of the chosen ternary plait point, the fitting points selected are spaced by $\Delta x_L = x_{L+1} - x_L = 0.005$. The first point corresponds to $L01 \equiv (0.570, 0.000)$ and, according to the plait point position, the number of fitting point $N_L$ varies in the range $20 \leq N_L \leq 25$.

- For the right branch of the binodal, i.e. for the compositions in the range between the 1-pentanol rich binary phase composition and that of the chosen ternary plait point, the fitting points are spaced by $\Delta x_R = 0.010$. The first point corresponds to $R01 \equiv (0.170, 0.000)$ and, according to the plait point position, this number of fitting point $N_R$ in the range $58 \leq N_R \leq 64$.

Through the PPLFM procedure for each fitting point a corresponding spinodal point is obtained. Details on the PPLFM method are reported in the previous papers.
5. RESULTS AND DISCUSSION

The results of the analysis are reported in Figure 2 where the spinodal points obtained for the different location of the plait point are reported; in the same graph it is also reported the binodal curve and the spinodal curve in a previous paper, [1], on the basis of the results obtained by using the experimental plait point \((x_P, y_P)\) instead than \((x_{0P}, y_{0P})\) location for the plait point. In the following we will analyze at first the effect of changing the location on the PP on the calculated spinodal points and at a later time the global effect on the spinodal curve.

In considering fitting points belonging to the left branch of the binodal we observe a clear even small effect of the plait point position; this effect is practically zero close to the plait point and increases as the fitting points composition approaches to the binary system. In particular if the plait point position is shifted towards right (i.e. \(x_P^{(\pm K)}\) increases) the spinodal points are shifted in the same direction; the largest variation between \(x_{P}^{(-2)}\) and \(x_{P}^{(2)}\) does result \(|\Delta x| \approx 0.02.\)

More complex is the situation observed by considering fitting points on the right branch of the REB; two well distinct trends can be detected. The first one, that goes through a pronounced maximum, starts from the plait point and ends more or less close to the abscissa axis depending on the \((x_{P}^{(\pm K)}, y_{P}^{(\pm K)})\) choice; in particular
by passing from \((x_p^{(-2)}, y_p^{(-2)})\) to \((x_p^{(+2)}, y_p^{(+2)})\) the distance of the last point belonging to this trend and the \(x\) axis increases. Beside the different \(x\) range observed for different plait point choices, the five trends do a complete overlap; this is a very interesting aspect that does not have an easy explanation and that we will try to clarify in a future paper. It is also to observe that, close to the chosen plait point, the spinodal points are, even if only slightly, above the REB; this is impossible because the spinodal curve must, by definition, be always internal to the binodal one just with a single point in common, the plait point. This means that, in that range, the solutions obtained with the PPLFM are non-physical; this result is not as worrying because it is evident looking at the trend of the physical solution around that in this range the spinodal points are practically coincident with the binodal. The second trend is observed, in a variable \(x\) range, close to the abscissa: in this ranges the spinodal points are almost vertical and depend on the choice of plait point.

At this point, knowing the coordinates of the theoretical spinodal points, the next step is to draw the spinodal curve. In the previous papers we showed that in drawing this curve it is necessary to take into account the spinodal compositions of the binary system containing the two partially soluble solutes (these compositions can be obtained independently by using the binary LLE data). In fact the ternary spinodal curve has to cross the \(x\) axis in correspondence of these two points; to respect this constrain we showed that part of theoretical spinodal points can not be used in the fitting. This is well illustrated in Figure 2. As can be seen in the figure, the simulated shift of the plait point does not affect the final drawing of the spinodal curve. In fact, regarding the left branch close to the plait point the spinodal curve passes through the spinodal points calculated at the five PPs, while more close the \(x\) axis the binary constrain forces the spinodal curve to pass at the left but not far away of the binodal points. Overall we can affirm that, in the water rich corner, the LLE data of the ternary system are fairly good described by the Generalized Wheeler-Widom-Huckaby Model. In fact, quite independently of the position of the plait point, the spinodal points determined according to the GWWHM are in fair agreement with the reasonable branch of the spinodal curve that connects the binary spinodal point located in the water rich corner and the plait point. More complex would be predict the shape of the right branch of the spinodal curve and then to make a comparison with the trend of the spinodal points determined according the GWWHM. For the right branch, starting from the plait point and moving to the right towards the binary system we obtained a large range \(x, x_P < x < 0.170\), where the spinodal points are independent of the plait point position. In the remaining range, close to the \(x\) axis, the spinodal points do depend on \((x_p^{(±K)}, y_p^{(±K)})\). In the range \(x_P < x < 0.170\) the spinodal points describe a curve with a high maximum with approximately coordinates equal \((x_{s\text{Max}}, y_{s\text{Max}}) \equiv (0.255, 0.260)\); this maximum is
close to that of the binodal curve at about \((x_{b\text{Max}}, y_{b\text{Max}})\) \(\equiv (0.235, 0.265)\). After the maximum the spinodal points decrease rapidly to zero. In this range, \(x_p < x < 0.170\), the spinodal curve can be drawn exclusively by interpolation of the binodal points because no constraints and no other information of the thermodynamic of the system are known. For \(x > 0.170\) the spinodal points curve to the left (this means that at increasing the abscissa of the fitting point the abscissa of the related spinodal point decreases). The resulting trend is in clear disagreement with that suggested by the composition of binary spinodal point in the 1-pentanol rich corner. Therefore, in this range of \(x\) the spinodal curve is drawn considering the descending trend present in the range \(x_p < x < 0.170\) and the constraint due to the binary spinodal point of the system water – 1-pentanol that impose the curve to pass through this point. As result of this, as can be seen clearly in the figure that no effect of the plait point position on the spinodal curve is present.

In conclusion, for different reasons, the fictitious change of the plait point position does not have effect on the spinodal curves. On the left branch this is in part because of the very small changes of the spinodal point positions at varying \((x_p^{\pm K}, y_p^{\pm K})\) and in part because of the effect of the binary spinodal point constraint. On the right branch a large part of spinodal curve is obtained by interpolation of spinodal points that are not affected by the plait point position, in the \(x\) range where this effect is present the trend of spinodal curve is determined essentially by the binary constraint. We are confident that a similar behavior is shown also by the other systems of the series water – 1-alcohol – 1-propanol whose LLE data we are using to obtain the respective spinodal curves; in fact the systems until now examined water – 1-butanol – 1-propanol, water – 1-pentanol – 1-propanol, water – 1-hexanol – 1-propanol, water – 1-octanol – 1-propanol, and water – 1-decanol – 1-propanol present very similar behaviors.

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