THE SPINODAL CURVE OF THE SYSTEM WATER – 1-BUTANOL – 1-PROPANOL ACCORDING TO THE WHEELER – WIDOM MODEL

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The spinodal curve of the system water – 1-butanol – 1-propanol has been determined, from the literature Liquid – Liquid – Equilibrium data (LLE), by using the Mean Field Approximation (MFA) on the Generalized Wheeler – Widom – Huckaby Model (GWWHM). The results are compared with those obtained for the system water – 1-pentanol – 1-propanol.

Key words: Ternary system, amphiphilic solvent, Wheeler-Widom model, spinodal curve.

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1. INTRODUCTION

The Liquid – Liquid – Equilibrium data (LLE) of a ternary system presenting a miscibility gap between the two solutes can be used to obtain the spinodal curve of the system by mean of the Generalized Wheeler – Widom – Huckaby Model (GWWHM) in the Mean Field Approximation (MFA) [1–8]. The original Wheeler – Widom model [1] considers a ternary system as constituted by three types of rod-like di-functional molecules, $AA$, $BB$, and $AB$, that occupy the bonds of a regular lattice with a single molecule for each bond. In this model, where $AA$ and $BB$ are the solutes and $AB$ is the amphiphilic solvent, the interactions $-A\cdot\cdot\cdotB-$ are forbidden ($\varepsilon_{AB} = \infty$), while the interactions $-A\cdot\cdot\cdotA-$ and $-B\cdot\cdot\cdotB-$ have the same energy ($\varepsilon_{AA} = \varepsilon_{BB} = 0$). At microscopic level, because only the interactions $AA\cdot\cdot\cdotAA$, $BB\cdot\cdot\cdotBB$, $AA\cdot\cdot\cdotAB$, and $AB\cdot\cdot\cdotBB$ may exist in solution, it follows that the sites of the lattice can be occupied only by $A$ ends or only by $B$ ends. The possibility to identify in the lattice sites $A$ and sites $B$ allows a direct analogy of this WW model with the Ising model, defined on the same lattice, where, at each site, the spin can be $1/2$ or $-1/2$.

At macroscopic level we can deduct for such a model the following characteristics:

1. The condition ($\varepsilon_{AB} = \infty$) implies that the two solutes are completely immiscible and then the binodal curve insists on the entire interval of binary composition.
This means, by using a Cartesian representation of the system with \( x = (X_3 - X_2)/\sqrt{3} \) and \( y = X_1 \) where \( X_1, X_2, \) and \( X_3 \) are respectively the mole fractions of the solvent and of the two solutes, that the binodal curve is defined in the whole range \(-1/\sqrt{3} \leq x \leq +1/\sqrt{3}\).

2. The possibility of the solvent to interact with both the solutes, by setting respectively interactions \( AA \cdots AB \) and \( AB \cdots BB \), increases the mutual solubility of the two solutes. Moreover the condition \( (\varepsilon_{AA} = \varepsilon_{BB} = 0) \) implies that the solvent, when added in small quantity to a mixture of the two solutes, is equally redistributed between the two ternary solutions in thermodynamic equilibrium. As a consequence of this the tie-lines are parallel to the \( x \) axis, the solubility gap is symmetrical and the plait point is coincident with the maximum of the binodal curve. For large concentration of the solvent the ternary system becomes homogeneous.

3. No effects of the temperature can be detected.

Although the model catches the main aspects of the phase equilibrium in ternary systems, it is too simplistic to describe real systems that usually present asymmetric binodal curves, tie-lines with slopes different from zero and temperature dependence. Several attempts to modify and extend the original model are present in literature \([2–8]\). The up-dated model used in this paper (GWWHM) accounts for a honeycomb lattice where two- and three-body interactions between the molecular ends exist at the lattice sites. This model is equivalent to the standard Ising model on a \( 3 \times 12 \) lattice and can be solved exactly to obtain the binodal curve \([3, 4]\); it allows describing systems with a non-zero solubility between the solutes, with asymmetric binodal curves, with tie-lines having slopes different from zero. This model can also account for binodal curve dependence on the temperature. Moreover it allows, by using the Mean Field Approximation, to obtain the spinodal curve of the system; in this case, for internal consistency, also the binodal curve must be determined within the same approximation.

The most important aspect of this model is that both the binodal and the spinodal curve can be described, in function of the composition of the system, by the same constant parameters \( \tau \) and \( \Delta \) that correspond respectively, in the Ising model, to the reduced temperature and to the asymmetry parameter. As a consequence of this, the calculation of the spinodal curve should be very simple. It would be sufficient to fit the experimental LLE data to the theoretical binodal GWWHM equation in order to obtain the values \( (\tau, \Delta) \); subsequently this parameters, inserted in the theoretical GWWHM spinodal equation, should allow obtaining the spinodal curve.

To test the possibility to predict, in this way, the spinodal curve starting from the LLE data we considered at first the system water (W) – chloroform (\( \text{CHCl}_3 \)) – acetic acid (AcH) \([9–11]\). Even if, by structural point of view, the species involved
in this system are very different from the rod-like molecules used by the models, the experimental solubility gap is very similar to that predicted by the original WW model. The reciprocal solubilities of water in pure chloroform and of chloroform in pure water are very small and then the binodal curve practically insists on the entire range of \( x \). The binodal is almost symmetrical with a flat maximum, the plait point is almost coincident with the maximum and tie-lines are almost parallel to the \( x \) axis. Despite these characteristics, after several attempts it was clear that the fit, to the GWWHM binodal equation, of the experimental binodal points in the entire binodal range of \( x \) gives poor results. For this reason we worked out a local fit procedure. The results obtained with this procedure were very good; the obtained spinodal passes through the plait point and was in very good agreement with the literature spinodal point of the system water–chloroform.

The reliability of the results obtained with the GWWHM model has been checked by the use of the mutual diffusion coefficients of system. In fact two spinodal compositions have been determined by using the thermodynamic condition that the determinant of the matrix of the diffusion coefficients of the system must be zero on the spinodal curve [12]. The four mutual diffusion coefficients \( D_{ij} \) have been determined, in the homogeneous region of the system, at two constant values of the mole fraction ratio \( X_{\text{W}}/X_{\text{CHCl}_3} \) and varying \( X_{\text{AcH}} \); by fitting the \( \| D_{ij} \| \) values vs. \( X_{\text{AcH}} \) the spinodal composition was chosen as that one for which \( \| D_{ij} \| = 0 \) [13, 14]. The agreement between the GWWHM prediction of the spinodal curve and the values obtained by the use of the diffusion technique was excellent.

Afterwards we considered systems constituted by water and two 1-alcohols with different chain length. In particular we took into consideration ternary system as HO-H – HO-(CH\(_2\))\(_n\)-H – HO-(CH\(_2\))\(_3\)-H with \( n = 4, 5, 6, \ldots \), for which LLE data are reported in literature [15–17]; in the following we will indicate this systems with the shorter notation HOH (2) – HOC\(_n\) (3) – HOC\(_3\) (1). In this system water and the 1-alcohol with the longer chain length are the solutes while 1-propanol is the solvent. The first terms of the \( n \)-alcohol series methanol, ethanol, and 1-propanol are completely miscible with water. For \( n \geq 4 \) the binary systems HOH – HOC\(_n\) present solubility gap [18]. The ternary systems HOH – HOC\(_n\) – HOC\(_m\) with \( m < n \) do not present a solubility gap if \( n = 1, 2, 3 \) and \( m = 1, 2, \ldots \). On the contrary a I type solubility gap is present if \( n \geq 4 \) independently on the value of \( m \) [19]. For both \( n \geq 4 \) and \( m \geq 4 \) a II type solubility gap should be present.

The molecular structure of the species involved in these systems is more like to that hypothesized by the WW and GWWH models. The hydrocarbon tail of the solvent and that of the alcholic solute are practically the same only differing in the number of C atoms; moreover it is proved by different techniques that the hydrocarbon tails of several classes of organic solutes (alcohols, diols, carboxylic acids, amines, etc.) interact each other by setting hydrophobic bonds also in dilute aque-
ous solutions [20–24]. On the other hand the hydroxyl group of the solvent is very similar to that of water and then the hydrophilic end of the solvent can easily set interactions also with the other solute of the system. In conclusion the solvent molecule can interact with one end with a solute and with the other end with the other solute according to the GWWHM model main hypothesis. It is to observe that solute – solute interactions are also possible via the –OH groups present in their molecules.

Regarding the general characteristics of the binodal curves of these systems we observe that the solubility of water in the long chain alcohol is always much larger than the solubility of the same alcohol in water; all the binodal curves are then shifted to one side of the Cartesian triangle graph. The curves are almost symmetric but the plait point, which is always on the left part of the curve, is distant from the maximum and the tie-lines close to the plait point are very steep.

Overall, these systems are very well suited to evaluate the applicability of the GWWHM in describing the properties of real ternary systems with a miscibility gap. In this paper we present the results obtained applying the GWWHM to the LLE experimental data of the system HOH (2) – HOCH₃ (3) – HOCH₃ (1); the data are reported in Figure 1.
2. EXPERIMENTAL "LLE DATA"

Under the heading "LLE data" two different types of experimental data are collected in literature: i) the composition of single binodal points and ii) the composition of the two conjugated phases in chemical equilibrium [25–27]. The compositions of single binodal point can be easily determined, with small errors, by the titration method. To a heterogeneous opalescent mixture of the two solutes the solvent is added drop by drop until the opalescence disappears; known the amount and the composition of the initial mixture and the quantity of solvent necessary to obtain a clear solution, the binodal composition can be calculated. The opposite procedure can also be used; to a homogeneous mixture of the solvent plus one solute the other solute is added drop by drop until the appearance of turbidity occurs. The composition of single binodal points are used to draw the binodal curve but do not provide complete information on phase equilibrium.

The determination of the compositions of the two conjugated phases requires more elaborate experiments. A ternary mixture belonging to the heterogeneous region is first stirred for a rather extended period and then allowed to separate in the two conjugated solutions; the time required for the separation can vary from few hours to 1 or 2 days for aqueous solutions of hydrocarbons. After standing, samples are taken from the individual phases and analyzed. The analytical determination can be carried out using a combination of various physical and chemical properties as refractive index, density, etc. or by direct determination of at least two components of the solution for example by means of gas – chromatography. If the physical – chemical properties are employed it is necessary the use of calibration curves. Usually the measurements required for the calibration curves can not be carried out at compositions close to the binodal curve and thus it is very often necessary to dilute the conjugated solutions to reach the composition range of validity of the calibration. Some other methods to determine the composition of the tie-line end points use additional turbidimetric titrations and eventually the knowledge of the binodal curve equation [28, 29]. As can be seen a much longer and more complicated procedure is necessary to obtain the composition of the conjugated solutions; as a consequence their compositions are usually affected by a larger error in respect to that of the single binodal ones.

Finally the plait point is obtained with a graphical method starting from the values of the conjugated compositions. Two conjugated compositions are connected by the "tie-line"; 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. 25 p. 278). It is evident that because the error on the
conjugate compositions and the interpolating procedure, even in presence of large $m$, the error on the composition of the plait point is not negligible. Ultimately, the ternary LLE that can be found in literature can be summarized as:

1. $N$ experimental binodal points $\left\{ (x_{b,i}^{\exp}, y_{b,i}^{\exp}) \right\}_{i=1,2,\ldots,N}$;

2. $m$ experimental tie-line end points $\left\{ (x_{(L),k}^{\exp}, y_{(L),k}^{\exp}), (x_{(R),k}^{\exp}, y_{(R),k}^{\exp}) \right\}_{k=1,2,\ldots,m}$

   where the subscripts $(L)$ and $(R)$ indicates that one end belongs, in respect to the plait point (PP) position, to the left branch of the binodal curve and the other to the right one;

3. The experimental plait point, $\left( x_{P}^{\exp}, y_{P}^{\exp} \right)$.

In facing the phase properties of a ternary system, it is useful to add to these data also the experimental binodal points relative to the binary system containing the two solutes. All these data of interest are reported for the system in exam in Figure 1.

### 3. THE LOCAL FITTING PROCEDURE

For the system water (W) – chloroform (CHCl$_3$) – acetic acid (AcH) the attempt to fit all together the experimental binodal points with the theoretical binodal equation of the GWWHM by using different couples of the parameters $(\tau, \Delta)$ failed because the agreement between the experimental and theoretical binodal was poor or just limited to some parts of the curve. Considering that this system presents characteristics of the binodal curve similar to that predicted by the original WW model it was easy to foresee that this behavior would have been general for almost all the systems. Therefore a different strategy was necessary. Because a better agreement between the experimental and theoretical binodal curve was obtained considering small range of the variable, a local fit was considered the winning strategy to face the problem.

The Local Fitting Procedure can be summarized as follows:

1. The set of the $N$ experimental binodal points, $\left\{ (x_{b,i}^{\exp}, y_{b,i}^{\exp}) \right\}_{i=1,2,\ldots,N}$ are fitted to a polynomial of suitable degree obtaining the representative experimental binodal curve (REB) with $y_{b}^{\exp}(x)$ equation. Generally in this fitting the $2 \cdot m$ experimental tie-line end points and the plait point compositions have not been used because these data have larger errors in respect to the single binodal points.

2. For some selected points of REB, $\left( x_{b,j}, y_{b,j} = y_{b}^{\exp}(x_{b,j}) \right)$ indicated as "fitting points" $F_j$, the equation $y_{b,j}^{th}(x)$ of the local theoretical binodal curve (thBj) that obeys to a predefined constraint is calculated. The choice of this constraint characterizes the fitting procedures; more details about this step are reported below.
This step requires the use of three parameters \( M_{b;j}, \tau_j, \Delta_j \) where \( M_{b;j} \) is a composition parameter dependent on \( x_{b;j} \).

3. By using the \((\tau_j, \Delta_j)\) parameters determined in step 2) the equation \( y_{th}^{s;j}(x) \) of the local theoretical spinodal curve (thSj) is calculated.

4. By using the \((M_{b;j}, \tau_j, \Delta_j)\) parameters the equation \( y_{th}^{t;j}(x) \) of the local theoretical tie-line, (thTLj) is also obtained.

5. The local spinodal point \((x_{s;j}, y_{s;j})\), that corresponds to \((x_{b;j}, y_{b;j})\), is then found as the intersection point of the two curves \( y_{th}^{s;j}(x) \) and \( y_{th}^{t;j}(x) \). In this procedure the parameter \( M_{s;j} \) is also determined.

6. At last the spinodal curve of the system is obtained by fitting the single spinodal points to a polynomial of suitable degree.

In step 2) for determining the parameters \( \tau_j, \Delta_j \) and \( M_{b;j} \) three independent equations are necessary. The first two are intuitive and impose that the theoretical
binodal has to pass through the selected point of REB. That is:

\[ x_{b;\alpha}^{th}(M_{b;j}; \tau_j, \Delta_j) = x_{b;j}, \]  
\[ y_{b;\alpha}^{th}(M_{b;j}; \tau_j, \Delta_j) = y_{b;j}, \]  

where \( \alpha = L, R \) depending if the binodal point belongs to the Right or to the Left branch of the curve (GWWHM has different equations for the two branches of the binodal). Obviously there are infinite theoretical binodal curves passing through the "fitting points" \( F_j \) but only one of these curves is necessary and sufficient to obtain the values of the three fitting parameters. Therefore it is possible to use different constraints to select a single theoretical local binodal curve; obviously it is convenient that the choice of the constraint is such that the resulting \((\text{thB}_j)\) has at least one property as similar as possible to the corresponding property of the (REB).

Until now three different procedures to obtain the spinodal curve from the LLE data according to the GWWHM model have been worked out. The first was indicated as GTLLFM (General Tie Line Local Fitting Method) [9, 14] because the third equation of step 2) imposes that the slope of the theoretical tie-line passing through the fitting point has to be as close as possible to the slope of the experimental tie-line passing through the same point. The second one was indicated as GSLFM (General Slope Local Fitting Methods) [10]; for this procedure the third equation imposes that the local slope of \((\text{thB}_j)\), calculated in \( F_j \), has to be as close as possible to the slope of (REB) calculated in the same point. Both these procedures have given poor results for the systems HOH (2) – HOC\(_n\) (3) – HOC\(_3\) (1) investigated until now. For this reason a new procedure has been proposed.

In this Plait Point Local Fitting Method (PPLFM) the third equation of step 2) imposes, for any fitting point \((x_{b;j}, y_{b;j})\), that the distance between the experimental plait point \( P \), \((x_{P;j}^\exp, y_{P;j}^\exp)\), and the local theoretical plait point \( P_j \), \((x_{P;j}^{th}, y_{P;j}^{th})\), must be minimum. Because at \( P_j \) it results \( M_j = 0 \) this implies:

\[ PP_j = \sqrt{[x_{b;\alpha}^{th}(0; \tau_j, \Delta_j) - x_{P;j}^\exp]^2 + [y_{b;\alpha}^{th}(0; \tau_j, \Delta_j) - y_{P;j}^\exp]^2} = \min . \]  

It is more convenient to express this condition in dimensionless form: to obtain this we divide equation 3 for the distance between the fitting point \( F_j \), \((x_{b;j}, y_{b;j})\), and the experimental plait point \( P \):

\[ \frac{PP_j}{PP} = \sqrt{[x_{b;\alpha}^{th}(0; \tau_j, \Delta_j) - x_{P;j}^\exp]^2 + [y_{b;\alpha}^{th}(0; \tau_j, \Delta_j) - y_{P;j}^\exp]^2} \]  
\[ \sqrt{[x_{b;j} - x_{P;j}^\exp]^2 + [y_{b;j} - y_{P;j}^\exp]^2} \]  

The elements involved in this procedure are illustrated in Figure 2.
4. RESULTS

For the system in exam the following LLE data are present in literature [15]:

1. $N = 27$ experimental binodal points $\{ (x_{b,i}^{exp}, y_{b,i}^{exp}) \}_{i=1,2,...,N}$;

2. $m = 3$ experimental tie-line end points, defined by the $x$ and $y$ coordinates: $\{ (x_{(L),k}^{exp}, y_{(L),k}^{exp}), (x_{(R),k}^{exp}, y_{(R),k}^{exp}) \}_{k=1,2,...,m}$ where the subscripts $(L)$ and $(R)$ indicates that one end belongs, in respect to the plait point (PP) position, to the left branch of the binodal curve and the other to the right one;

3. the experimental plait point, $(x_P^{exp}, y_P^{exp})$;

4. the experimental binodal compositions relative to the binary system HOH (2) – HOC₄ (3) [31].

The experimental data are reported in Figure 1. In the PPLFM only the binodal point and the plait point compositions are necessary [30]. The $N' = 27 + 2$ binodal points have been fitted to a forth degree polynomial imposing that the curve has to pass through the experimental plait point and the binary binodal points; the interpolating function, REB, is reported in the figure.
In applying the PPLFM procedure we used a large set of fitting points that, because the plait point position is known, have a definite belonging either to the physical left branch or to the physical right branch of the binodal curve. In particular we have used 109 points for the left branch and 238 for the right branch of the binodal.

For each \((x_{b,j}, y_{b,j})\) binodal fitting point we have, as result of the procedure, the values of parameters \(\tau_j, \Delta_j\), of the variable \(M_j\), and the composition of the corresponding spinodal point \((x_{s,j}, y_{s,j})\). We can also calculate the composition of the theoretical plait point \(P_j\) that minimizes equation 4.

Because of the use of the local fitting procedure the parameters \(\tau_j\) and \(\Delta_j\) can change on the binodal composition and their variation on \(x\) has not any constrain and is not very significant. Differently the new variable \(M_j\) has defined limits: in fact for each branch the following limits hold

\[
0 \leq M \leq M_{\text{max}} \quad \left\{ \begin{array}{l}
M = 0 \quad \rightarrow \text{theoretical plait point;} \\
M = M_j^{(\alpha)} \quad \rightarrow y_j^{(\alpha)} = 0 \quad \text{(binary limit)}.
\end{array} \right.
\]

While the \(M_j^{(\alpha)}\) do not assume definite values the condition \(M = 0\) at the experimental plait point must be fulfilled. We can use the respect of this condition to evaluate the reliability of our results.
Fig. 5 – Local theoretical plait point coordinates; —— representative experimental binodal (REB), ○ experimental plait point (P), • fitting point $F_j$ in the range $-0.494 \leq x_{F_j} \leq -0.468$, ● corresponding $P_j$ in the range $-0.468 \leq x_{P_j} \leq -0.468$, ■ fitting point $F_j$ in the range $-0.468 \leq x_{F_j} \leq -0.429$, ■ corresponding $P_j$ in the range $-0.471 \leq x_{P_j} \leq -0.468$.

In Figure 3 the $M_j$ values are reported as a function of $x$; the definition range of $M_j$ is also indicated with two vertical line passing through the binodal points of the binary system HOH (2) – HOCH$_4$ (3). As it can be observed in the graph in the right branch of the curve there are at least two discontinuities; similar behavior is observed for the trend of the parameters $\tau_j$ and $\Delta_j$ when reported versus $x$. However the curve is strictly decreasing in the left branch and strictly increasing in the right one as expected. In Figure 4 is reported a zoom of the previous graph for $x$ values in the neighborhood of the plait point; the experimental composition $(x_P, y_P)$ is also reported. Interpolating, with a straight line, separately the last nine points relative to the left branch and the first nine relative to the right one we obtain an excellent agreement between the $x$ value that correspond for both the branches at $M = 0$, $x = -0.4680$, and the experimental composition of the plait point $(x_P = -0.4679, y_P = 0.900)$. It is worth noting that for the other two procedures the condition $M = 0$ at the experimental PP is not fulfilled.

It is also interesting to analyze how the $P_j$ position changes as a function of $x$ along the binodal curve. In Figures 5 and 6 the $P_j$ coordinates are reported for some selected set of fitting points of the binodal curve. In particular in Figure 5 the two
selected portions of the REB belong one to the left branch and the other to the right branch of the curve and both include the experimental plait point. In Figure 6 the two selected portions belong to the right branch of REB. It is interesting to observe that, while for the left branch of binodal the local theoretical plait points are always located under the REB, for almost all the right branch, excluded a very limited portion of REB, the theoretical plait points are outside the binodal curve. Obviously there is not any constrain that imposes $P_j$ to be internal to the REB but we have never found for the other examined systems a similar behavior. This anomaly seems to be related to the high asymmetry of the binodal curve with the plait point very far from the maximum of the curve; this aspect will be analyzed in details in another paper. This unexpected behavior of the theoretical plait point also influences the spinodal point compositions. The spinodal ternary points are reported in Figures 7, 8 and 9 as well as the spinodal binary points of the system HOH (2) – HOCl (3); these last data have been computed using the NRTL (Non Random Two Liquids) model and the corresponding constant present in literature [18].
To analyze the spinodal curve we consider three different ranges of $x$: the first corresponds to the left branch of REB, the second and the third to two consecutive ranges of the right branch. We can make the following observations:

1. Regarding the left branch of the binodal curve we observe that the corresponding spinodal points have a reasonable trend. They tend to the binodal curve approaching the plait point and moreover they are in a fairly good agreement with the binary spinodal point; the deviation observed at low concentration HOCH$_3$ are probably due to the inability of the GWWHM to gives good results close to the binary limit. Then it is rather easy to draw this section of the spinodal curve just interpolating the spinodal points, the plait point, and the binary spinodal point, see Figure 7.

2. The first range of the right branch is defined by $-0.4679 \leq x \leq -0.35$ where $x = -0.4679$ corresponds to the plait point abscissa. In this range the spinodal points are outside the binodal curve, see Figure 8; this has no physical sense because the spinodal points must be by definition inside the binodal curve. It is easy to deduct that this unphysical result derives from the previously illustrated behavior of the theoretical plait point. Because all the obtained spinodal points
must be rejected as unphysical we could not draw the spinodal curve in this range of $x$; however looking at the general trend of the spinodal points it is reasonable to predict that in this range the spinodal curve is practically coincident with the binodal one.

3. In this range of composition the spinodal points are inside the binodal curve and then they are significant by physical point of view. However we remind that also these spinodal points, as those of the previous range, derive form theoretical spinodal curves whose plate points were outside the experimental binodal curve. This anomaly seems to influence the trend of the spinodal points; in fact they result not to be in good agreement with the binary spinodal point, see Figure 9. Ultimately the fitting of the spinodal points does not permit to draw a significant spinodal curve. We could guess a reasonable spinodal curve using, in the polynomial fitting, only the set of spinodal points close to the maximum and imposing that the polynomial has to pass through the binary binodal point.
5. CONCLUSIONS

In this paper we have presented the result of the analysis of the LLE data for the system \( \text{HOH} \) (2) – \( \text{HOC}_4 \) (3) – \( \text{HOC}_3 \) (1) using the GWWHM. The binodal curve of the examined system is, in the triangle diagram, completely shifted towards the pure water corner accounting for the low solubility of 1-butanol in pure water and the much higher solubility of water in pure 1-butanol. The binodal curve is highly asymmetric and the tie lines have a high slope, see Figure 1. The PPLFM has given very good results for the left branch of the binodal, while, for the right branch, has given unphysical result for a long piece of the binodal close to the plait point and almost poor results for the remaining part. However, with the help of the spinodal points of the binary system \( \text{HOH} \) (2) – \( \text{HOC}_4 \) (3), a reasonable spinodal curve can be drawn, see Figure 10.

If we compare this figure with Figure 11 where the binodal and spinodal curves are reported for the companion system \( \text{HOH} \) (2) – \( \text{HOC}_5 \) (3) – \( \text{HOC}_3 \) (1) [30] we observe some similarities.

In both the systems the spinodal curve is practically coincident with the binodal one for a long section of the right branch just after the plait point; a preliminary
analysis of the LLE data for the system HOH (2) – HOCl (3) – HOCl (1) confirms this behavior also for this system. The water rich metastable region is small while the alcohol rich metastable region is very large. This is very interesting because it should makes possible to run diffusion experiments in the right metastable region; it is worth reminding that the knowledge of the diffusion coefficients in these regions is a fundamental parameter in any phase separation model.

Finally it is to observe that the $y_{b,\text{max}}$ is much closer to the $y_{b,\text{max}}$ in the case of system HOH (2) – HOCl (3) – HOCl (1) than in case of HOH (2) – HOCl (3) – HOCl (1); this trend seems to be confirmed by the preliminary analysis of the system HOH (2) – HOCl (3) – HOCl (1).

In the next future this analysis will be extended to systems containing as solutes 1-alcohols with $n = 7, 8, 9, 10$ to see the effect of much longer hydrophobic chains on the shape of the spinodal and on the extension of the metastable area.
Fig. 11 – System HOH (2) – HOC₅ (3) – HOC₃ (1); - - - - representative experimental binodal (REB), ● experimental plait point (P), ■ spinodal point of the binary system HOH (2) – HOC₅ (3), □ ternary spinodal points, —— interpolated spinodal curve.

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REFERENCES