THE USE OF THE WHEELER – WIDOM MODEL TO COMPUTE THE SPINODAL CURVE OF THE SYSTEM WATER – 1-HEXANOL – 1-PROPAANOL

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

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

1. INTRODUCTION

The liquid – liquid extraction is a basic chemical separation procedure very frequently used in the research chemical laboratories as well as in the industrial plants [1, 2].

With this procedure a solute, component 1, dissolved in a solvent, component 2, is extracted or pulled from this liquid phase (1 + 2) by using another solvent, component 3, insoluble or partially soluble with component 2, in which the solubility of component 1 is larger than in 2. The liquid – liquid elementary operation is illustrated in Figure 1 by using the typical representation of the phase equilibrium for a ternary system exhibiting a solubility gap between two components; we use the Cartesian representation of the ternary system for which the following relations hold:

\[ x = \frac{X_3 - X_2}{\sqrt{3}} \]

\[ y = X_1 \]

where \( X_i \) with \( i = 1, 2, 3 \) is the mole fraction of component \( i \). According to Figure 1, component 1 is completely miscible with both components 2 and 3, while 2 and 3 are only partially miscible each other; component 3 has a low solubility in component 2 while component 2 is quite soluble in component 3. In particular the binary system (2 + 3) presents a solubility gap for compositions between points \( H \) and \( I \), \( x_H \leq x \leq x_I \); any binary mixture in this range will separate in two phases with com-
positions $x_H$, the phase rich in component 2, and $x_I$, the phase rich in component 3. By adding component 1 to a heterogeneous mixture (2 + 3), the mutual solubility of components 2 and 3 increases and the compositions of the ternary solutions in thermodynamic equilibrium describe the so called binodal or coexistence curve that divides the ternary diagram in two regions, namely the homogeneous one-phase and the heterogeneous two-phase regions. The segments joining the conjugate compositions in equilibrium along the binodal curve are called tie-lines; if component 1 is equally distributed between the two ternary solutions in thermodynamic equilibrium, the tie-lines are parallel to $x$ axis otherwise they could have positive or negative slopes. The plait point, not shown in the figure, is the point where the two solutions in thermodynamic equilibrium coincide and then the corresponding tie-line is tangent to the binodal curve [3, 4].

Let the initial composition of the binary system (1+2), from whom the component 1 must be extracted, be indicated as $A$. By adding component 3, the composition of the system will move, according to the amount of added 3, along the segment that connects $A$ and the corner of the triangle that corresponds to pure component 3. If the new composition $B$ is inside the solubility gap the heterogeneous mixture will separate in two homogeneous solutions in thermodynamic equilibrium; the composition of this two conjugated solutions, $C$ and $D$ in the figure, depends on the composition of $B$ and on the slope of the tie-line passing through $B$. As can be observed in the figure, this first extraction step leads to a ternary $D$ solution that contains a small amount of component 3 and an amount of component 1 that is almost one half of that initially present in solution $A$. If solution $D$ is taken apart from the conjugated
solution $C$, a second extraction can be performed leading to the composition $G$ in the figure. Repeating this procedure the composition of the phase rich in component 1 will move down along the binodal curve approaching to the point $H$ that corresponds to a binary $(2 + 3)$ system with no component 1 and a very small amount of component 3; the extraction of component 1 from the initial solution $A$ is then completed. The extraction process, illustrated here as a discontinuous succession of similar steps, can be also performed in continuum with high throughput and much lower costs.

It is evident that in planning an extraction procedure the knowledge of phase diagram of the ternary system containing the species that must be extracted, component 1, and the two solvents, components 2 and 3, is mandatory. Beside the thermodynamics of the system also the kinetic aspects are important. In fact the phase separation mechanism, and then its kinetic, can be very different inside the two-phase region of the system. This is because the presence of the so called "spinodal curve" that, having in common with the binodal the plait point, creates in the two phase region three separated areas. In the two areas delimited by the binodal and the spinodal curves, one on the left and the other on the right of the plait point, the system is metastable and the phase separation, occurring trough a "nucleation" and a "growth" mechanism that requires large concentration fluctuations, could be very slow. In the region under the spinodal curve the system is unstable and the phase separation happens even with small fluctuations; this process is then very rapid interesting suddenly the whole system [5].

Unfortunately, while the binodal curve can be easily experimentally determined the spinodal curve can not be simply obtained. The relative position of the binodal and spinodal curves is very important for all the separation processes and also in the extraction procedure described here; in fact, if their positions were be known, the addition of pure component 3 could be modulated to obtain a $B$ composition in the unstable region thus obtaining an instantaneous phase separation.

Very recently some of us have determined the spinodal curve of the systems water – 1-butanol – 1-propanol and water – 1-pentanol – 1-propanol starting by literature liquid – liquid – equilibrium (LLE) data [6, 7]. The LLE data of these systems are a part of a more extensive study focused on the determination of the phase equilibrium data for the systems water – 1-alcohol – 1-propanol. The interest in the thermodynamics of these systems is due to the possibility to use the alcohols with long hydrophobic chain as solvents in the extraction of 1-propanol from its aqueous solutions [8–10]. In fact, 1-propanol and water form a minimum azeotrope at $T = 360.15$ K and their separation using distillation method is unfeasible from an economical point of view; the extraction technique is then the best method for the separation of these two substances. Obviously, among all the "organic solvents", the alcohols with long hydrophobic chains are good candidates as "extracting solvents" for this procedure.
In this paper we present the result of a study undertaken to determine the spinodal curve of the system water – 1-hexanol – 1-propanol starting by the LLE experimental data, reported in Figure 2, and using the Wheeler and Widom model for solutions containing two partially insoluble solutes and an amphiphilic solvent.

2. THE WHEELER–WIDOM MODEL

The Wheeler–Widom Model (WWM) considers a model ternary system as constituted by three types of bi-functional rod-like molecules $AA$, $BB$, and $AB$ where $AA$ and $BB$ are the solutes (the partial miscible components) and $AB$ is the amphiphilic solvent (the component in which both $AA$ and $BB$ are soluble). The molecules are supposed to cover completely the bonds, one molecule per bond, of a regular lattice. The interaction $-A \cdots B-$ are forbidden while the interactions $-A \cdots A-$ and $-B \cdots B-$ have the same energy; this implies that only $A$ or only $B$ ends may meet at a given lattice site and that the amphiphilic solvent sets equal interactions with the two solutes. The model reduces to the standard Ising model.
(with spins 1/2 and only nearest-neighbor interactions) on the same lattice, its ferromagnetic transition corresponding to the phase separation in the molecular system\cite{11}.

By macroscopic point of view the model foresees a complete insolubility between the solutes, with a solubility gap that insists on the whole $x$ range, tie-lines parallel to the $x$ axis, a binodal curve symmetrical, and a plait point coincident with the maximum of the curve. Although the simple initial model catches the mains aspect of the phase separation, it lacks elements that could describe real systems. Successive modifications of the model led to the current Generalized Wheeler – Widom – Huckaby Model (GWWHM) that in the Mean Field Approximation (MFA) can be adapted to real systems [12–18]. This model supplies the equations for the two characteristic curves, the binodal and the spinodal one. These equations are described by functions which depend on two parameters $\tau$, $\Delta$ and on the variable $M$ that generates the curves; the quantities $\tau$, $\Delta$ and $M$ correspond, respectively, to the reduced temperature, to the asymmetry parameter, and to the magnetization of the associated Ising model.

The theoretical binodal is described for each branch of the curve, in respect to the plait point position, by the parametric equation:

\[
\{x_{b,\alpha}^{th}(M_b; \tau, \Delta), y_{b,\alpha}^{th}(M_b; \tau, \Delta)\} \quad \text{with } (\alpha = L, R),
\]

where $\tau$ and $\Delta$ are parameters, both fixed for a specific binodal, and $M_b \in [0, M_{Max}^{(b,\alpha)}]$ is the variable that describes the binodal, $M_b = 0$ corresponds to the plait point while $M_b = M_{Max}^{(b,\alpha)}$ corresponds to the binary systems; L and R indicate the Left and Right branches originated by the plait point. Analogously the theoretical spinodal is described for each branch by the parametric equation:

\[
\{x_{s,\alpha}^{th}(M_s; \tau, \Delta), y_{s,\alpha}^{th}(M_s; \tau, \Delta)\} \quad \text{with } (\alpha = L, R),
\]

where $\tau$ and $\Delta$ are the same than in binodal equation while $M_b \neq M_s$. Analogously for $M_s$ the following limits hold $M_s \in [0, M_{Max}^{(s,\alpha)}]$; in particular $M_s = 0$ corresponds to the plait point while $M_s = M_{Max}^{(s,\alpha)}$ corresponds to the binary systems.

The theoretical plait point is the common end-point of the two binodal branches, Left and Right, corresponding to the vanishing value of the variable $M_b$; therefore,

\^In systems where the mole fraction of each component may change in the all range $0 \leq X_i \leq 1$ the concept of solvent and solute, being correlated to the relative amount of the components, loses completely its meaning. It is interesting to notice that in this model the concept of solvent and solutes refers to the structure of the species in solution. Component $AB$, even in small amount in respect to component $AA$, $BB$ or both, maintains its characteristic of solvent because it is the only component able to interact with all the others present in solution.
the coordinates of the theoretical plait point are:

\[
\begin{align*}
    x_P &= x_{b,\alpha}^{th}(0; \tau, \Delta) \\
    y_P &= y_{b,\alpha}^{th}(0; \tau, \Delta)
\end{align*}
\]

where \((\alpha = L, R)\).

The plait point corresponds also to \(M_s = 0\) and then:

\[
\begin{align*}
    x_P &= x_{s,\alpha}^{th}(0; \tau, \Delta) \\
    y_P &= y_{s,\alpha}^{th}(0; \tau, \Delta)
\end{align*}
\]

Finally, the theoretical tie-line, corresponding to a theoretical binodal, is the straight line that connects a generic binodal point of the left branch, with \(M_b^{(L)}\), to the point of the right branch with the same value of the concentration variable \(M_b^{(R)} = M_b^{(L)}\).

The compositions of the tie-line end points are:

\[
\begin{align*}
    x_{b,L} &= x_{b,L}^{th}(M_b^{(L)}; \tau, \Delta) \\
    y_{b,L} &= y_{b,L}^{th}(M_b^{(L)}; \tau, \Delta) \\
    x_{b,R} &= x_{b,R}^{th}(M_b^{(R)}; \tau, \Delta) \\
    y_{b,R} &= y_{b,R}^{th}(M_b^{(R)}; \tau, \Delta)
\end{align*}
\]

and then, indicating \(M_b^{(L)} = M_b^{(R)} = M_{11}\), the theoretical tie-line slope is

\[
s_{11}^{th}(M_{11}; \tau, \Delta) = \frac{y_{b,R}^{th}(M_{11}; \tau, \Delta) - y_{b,L}^{th}(M_{11}; \tau, \Delta)}{x_{b,R}^{th}(M_{11}; \tau, \Delta) - x_{b,L}^{th}(M_{11}; \tau, \Delta)}.
\]

The two equivalent tie-line equations are then:

\[
\begin{align*}
    y_{11}^{th}(x; M_{11}, \tau, \Delta) &= y_{b,L}^{th}(M_{11}; \tau, \Delta) + s_{11}^{th}(M_{11}; \tau, \Delta)(x - x_{b,L}^{th}(M_{11}; \tau, \Delta)) \\
    y_{11}^{th}(x; M_{11}, \tau, \Delta) &= y_{b,R}^{th}(M_{11}; \tau, \Delta) + s_{11}^{th}(M_{11}; \tau, \Delta)(x - x_{b,R}^{th}(M_{11}; \tau, \Delta)).
\end{align*}
\]

The knowledge of the quantities \((M, \tau, \Delta)\) does permit to obtain all the characteristic parameters of the solubility gap. Thus it would seem very easy to obtain the spinodal curve of a generic system by the knowledge of the corresponding LLE data. The fitting of the theoretical binodal equation to the experimental binodal data should permit to obtain the quantities \((M, \tau, \Delta)\) and then the spinodal curve as well as all the other characteristic parameters of the system.

3. THE LOCAL FITTING METHOD

Actually the GWWH model, if applied to the LLE data in the entire \(x\) range that underlies the solubility gap, does not give reliable results even for systems whose solubility gap is very similar to that predicted by the original WWM; this is the case of the system water – chloroform – acetic acid. The model gives pretty good results
only if it is applied to small section of the experimental binodal curve. From this observation it was developed the so called Local Fitting Method described below [19].

This method starts by fitting the experimental binodal points to a polynomial of suitable degree; the result of this fit is the equation $y_{\text{exp}}(x)$ also indicated with REB, acronym for Representative Experimental Binodal. It is then possible to choose a set of $n$ point located on the REB $(x_{b,j}, y_{b,j} = y_{\text{exp}}(x_{b,j}))$ with $j = 1, 2, \ldots, n$ that will be indicated as FPS for Fitting Point Set.

The local fitting method means to associate to each $(x_{b,j}, y_{b,j})$ a theoretical binodal point. Since this point is characterized by the three quantities $(M, \tau, \Delta)$, the fitting procedure implies to define three theoretical conditions, so that, from these conditions it will follow the value of the theoretical quantities corresponding to the representing experimental characteristic of the fitting point. The three fitting conditions can be chosen as it follows. The first two are intuitive and impose that the theoretical binodal has to pass through the selected fitting point of REB. That is:

\begin{align*}
    x_{b,j}^{\text{th}}(M_{b,j}; \tau_j, \Delta_j) &= x_{b,j}, \quad (7) \\
    y_{b,j}^{\text{th}}(M_{b,j}; \tau_j, \Delta_j) &= y_{b,j}. \quad (8)
\end{align*}
Fig. 4 – $F_j$ and $P_j$ coordinates at different $j$ values; $\bullet$ $F_j \equiv (x_{b,j}, y_{b,j})$, $\bigcirc$ $P_j \equiv (x_{P_j}^{th}, y_{P_j}^{th})$, ■ representative experimental plait point.

where $\alpha = L, R$ depending if the binodal point belongs to the Right or to the Left branch of the curve. The third condition depends on the specific method of fitting; it is generally a condition for the theoretical binodal coordinates related to a property of the fitting point, expressed in terms of the representative experimental quantities. It can be written as:

$$\phi_{b,j}^{th}(M_{b,j}; \tau_j, \Delta_j) = \xi_j.$$  \hspace{1cm} (9)

Since equations (7), (8) and (9) are known functions, they form a system of transcendental equations having as solution the quantities $(M_{b,j}, \tau_j, \Delta_j)$; also $\alpha_j$ is obtained in this procedure. Thus for each fitting point it is possible to obtain, by using the equations reported above, the local theoretical binodal curve (thBj), the local theoretical spinodal curve (thSj), and the local theoretical tie-line (thTLj). The local theoretical spinodal point, $(x_{s,j}^{th}, y_{s,j}^{th})$, that corresponds to the fitting point with coordinates $(x_{b,j}, y_{b,j})$ is then obtained as the intersection point of the local theoretical spinodal curve (thSj) and the local theoretical tie-line (thTLj). Finally the global spinodal curve is obtained by fitting to a polynomial of suitable degree all the local theoretical spinodal points.

Until now three different local fitting procedures have been worked out; they differ, as said above, for the nature of equation (9). The first procedure indicated as
Computation of the spinodal curve of water–1-hexanol–1-propanol

GTLLFM (General Tie Line Local Fitting Method), imposes as third equation that the slope of the theoretical tie-line must be equal (if $K_j = 1$), or almost equal (if $K_j \approx 1$), to the slope of the experimental tie-line in the same point:

$$s_{th}^{tl,j}(M_{b,j}; \tau_j, \Delta_j) = K_j s_{exp,j}.$$

(10)

This procedure has given very good result for the system water – chloroform – acetic acid but poor results when applied to the systems water — 1-alcohol — 1-propanol [19–21]. To analyze these last systems a second procedure was developed [22, 23]; this procedure indicates as GSLFM (General Slope Local Fitting Method) imposes as Equation (9) that the slope of the theoretical binodal must be equal (if $K_j = 1$), or almost equal (if $K_j \approx 1$), to the slope of the representative experimental binodal in the same point:

$$d_{y_{th,b}}(M_{b,j}; \tau_j, \Delta_j) = K_j d_{y_{exp,b}}(x) \bigg|_{x=x_j}.$$

(11)

Also this procedure gave good results if applied to the system water – chloroform – acetic acid but poor results for the systems water – 1-alcohol – 1-propanol [22, 23].

A third procedure was then developed; in this Plait Point Local Fitting Method
(PPLFM) the third equation imposes that the distance between the experimental plait point $P$, $(x^{\exp}_P, y^{\exp}_P)$, and the local theoretical plait point $P_j$, $(x^{\text{th}}_P, y^{\text{th}}_P)$, must be minimum. This results in:

$$
PP_j = \sqrt{\left( x^{\text{th}}_b,\alpha(0;\tau_j,\Delta_j) - x^{\exp}_P \right)^2 + \left( y^{\text{th}}_b,\alpha(0;\tau_j,\Delta_j) - y^{\exp}_P \right)^2} = \text{min} \quad (12)
$$

because at $P_j$ it results $M = 0$. This condition can be more conveniently expressed in a dimensionless form by dividing equation (12) for the distance between the fitting point $F_j$, $(x_{b,j}, y_{b,j})$, and the experimental plait point $P$:

$$
\frac{PP_j}{PF_j} = \frac{\sqrt{\left( x^{\text{th}}_b,\alpha(0;\tau_j,\Delta_j) - x^{\exp}_P \right)^2 + \left( y^{\text{th}}_b,\alpha(0;\tau_j,\Delta_j) - y^{\exp}_P \right)^2}}{\sqrt{\left( x_{b,j} - x^{\exp}_P \right)^2 + \left( y_{b,j} - y^{\exp}_P \right)^2}} = \text{min} \quad (13)
$$

This procedure has given valuable results when applied to some water – 1-alcohol – 1-propanol systems [6, 7].

4. RESULTS

For the system in exam the following LLE data are present in the literature [8]:

![Spinodal points vs. x](image-url)
1. \( N = 39 \) experimental binodal points \( \{ (x_{b,i}^{\text{exp}}, y_{b,i}^{\text{exp}}) \}_{i=1,2,...,N} \);

2. \( m = 3 \) experimental tie-line end points, defined by the \( x \) and \( y \) coordinates:
   \( \{ (x_{(L),k}^{\text{exp}}, y_{(L),k}^{\text{exp}}); (x_{(R),k}^{\text{exp}}, y_{(R),k}^{\text{exp}}) \}_{k=1,2,...,m} \);

3. The experimental plait point, \( (x_P^{\text{exp}}, y_P^{\text{exp}}) \);

4. The experimental binodal compositions relative to the binary system water – 1-hexanol [24].

In the following we will indicate the elements of the 1-alcohols series, \( \text{HO}-(\text{CH}_2)_n-\text{H} \) with \( n = 1,2,\cdots \), as \( \text{HOC}_n \). So we will use for water – 1-hexanol – 1-propanol the shorter notation \( \text{H}_2\text{O}–\text{HOC}_6–\text{HOC}_3 \).

Because the PPLMF does not use the tie-lines, only the experimental binodal points and the experimental plait point are reported in Figure 2; the points with \( y = 0 \)
are relative to the binary system water – 1-hexanol. The binodal points have been fitted to a forth degree polynomial imposing that the curve has to pass through the experimental binary binodal points [24]; the interpolating function, REB, is reported in the figure. Because the REB does not exactly pass through the Experimental Plait Point (EPP), the Representative Experimental Plait Point (REPP) has been constructed. Considering the position of the plait point, on the left of the maximum of the binodal curve, and considering that the experimental error on the plait point coordinates are almost the same, the REPP is determined as the intersection point between the REB and the straight line passing through the EPP and parallel to the negative bisector. In using the PPLFM the REPP coordinates have been used.

The set of fitting points were uniform defined, as the horizontal distance between two successive points is $\Delta x = 0.001$. The left binary limit has the coordinate $x_L = -0.5761$, the right binary limit has the coordinate $x_R = 0.2425$, and the plait point has the coordinate $x_P = -0.4545$. Therefore, we used $N_f = 820$ fitting points, on the left branch the fitting points have coordinates $\{x_j\}_j^{(L)}$, $1 \leq j \leq 124$ and the fitting located on the right branch have the coordinates $\{x_j\}_j^{(R)}$, $125 \leq j \leq 820$.

The output of the PPLFM procedure gives, for each fitting point $(x_b,j, y_b,j)$, the following quantities: $\tau_j, \Delta_j, M_{b,j}$, $(x_{th,j}^L, y_{th,j}^L)$, $(x_{th,j}^R, y_{th,j}^R)$ . Because the meaning of the local fitting procedure we do not expect that the parameters $\tau_j$ and $\Delta_j$ have constant values on $x_j$; in fact they show not easily predictable trends sometimes with sudden discontinuities. On the contrary, $M_{b,j}$ must have a definite dependence on $x_j$ because the following restrictions must be respected:

\[
0 \leq M_{b,\alpha,j} \leq M_{\text{Max}}^{(b,\alpha)} , \quad \begin{cases} 
M_{b,\alpha,j} = 0 & \text{theoretical plait point} , \\
M_{b,\alpha,j} = M_{\text{Max}}^{(b,\alpha)} & y_{b\alpha} = 0 \text{ (binary limit)} .
\end{cases}
\]

Thus, indicating with $(x_{b,L}^{\text{exp}}, 0)$ and $(x_{b,R}^{\text{exp}}, 0)$ the composition of the two binary binodal points, the following conditions must be fulfilled:

\[
x_{b,L}^{\text{exp}} \leq x_j \leq x_P , \quad M_j \text{ is a strictly decreasing function of } x_j , \quad M_{\text{Max}}^{(b,L)} \geq M_j \geq 0 ,
\]

\[
x_j = x_P , \quad M_P = 0 ,
\]

\[
x_P \leq x_j \leq x_{b,L}^{\text{exp}} , \quad M_j \text{ is a strictly increasing function of } x_j , \quad 0 \leq M_j \leq M_{\text{Max}}^{(b,R)} .
\]

The obtained values of $M$ are reported as a function of $x$ in Figure 3. A very strange behavior can be observed in the figure. Regarding the left branch we observe a strictly decreasing trend of $M$ that goes to zero for an $x$ value very close to that of the PEPP. On the contrary an anomalous behavior is evident on right branch. In fact, for a large range of $x$ that starts close to $x_j \approx x_P$, $-0.451 \leq x \leq -0.228$ the system of equations (7), (8) and (13) has not solutions, moreover in the range $-0.227 \leq x \leq 0.243$ the $M_j$ values increase with $x$, as expected, but assuming a value close to
zero at $x \approx -0.227$ abscissa that is very different from that of the representative plait point.

A peculiar behavior can be observed also in the trends of the \((x_{P_j}^{th}, y_{P_j}^{th})\) at varying \(x_j\). The data relative to the left branch are reported in Figure 4 and those relative to the right branch in Figure (5). In Figure (4) is reported a portion of the REB that includes all the left branch and the plait point and for some selected fitting points $F_j, (x_{b,j}, y_{b,j})$, the correspondent theoretical plait point $P_j, (x_{P_j}^{th}, y_{P_j}^{th})$; as it can be seen as the fitting points approach REPP also the theoretical plait points approach, as expected, the same value. In Figure 5 the data relative to the $x$ range $-0.227 \leq x \leq 0.243$ of the right branch of REB are reported; it is to observe that, decreasing $j$ to $j = 350$ then approaching to $x_{350} = -0.227$, the value of the theoretical plait point tends to the fitting point, i.e. $P_j \rightarrow F_j$. This is an anomaly never found in the analysis of the other systems, because $F_{350}$ seems to behave as a "plait point".
Finally the composition of the spinodal points is reported in Figure 6. From this figure we observe that the lack of the spinodal points in the range $-0.451 \leq x \leq -0.228$ is not very important in drawing the global spinodal curve; similarity with the other investigated systems, and the trends of the $(x_{s,j}^{th}, y_{s,j}^{th})$ in the other ranges of $x$, strongly suggest that in this $x$ range the spinodal and the binodal curves are practically coincident. The spinodal points seem also to be in fairly good agreement with the binary spinodal points calculated by the literature NRTL coefficients [24]; the curved trend observed at low $y$ value has been found for all the examined system and is indicative of a poor capability of the model to describe systems at low solvent concentration.

The spinodal curve obtained by interpolation of the theoretical spinodal points for $y > 0.10$ with the constrain to pass through the binary spinodal points is reported in Figure 7; for comparison the spinodal curves of the systems water – 1-butanol – 1-propanol and water – 1-pentanol – 1-propanol are reported in Figures 8 and 9.
5. DISCUSSION AND CONCLUSIONS

The comparison of Figures 7, 8 and 9 permits a first semi-quantitative analysis of the phase equilibrium properties of these systems. In this analysis we will use the following notations; $A_{1Ph}$ is the area of the one phase region, $A_{2Ph}$ is the area of the two phase region, $A_{meta}$ is the area of the metastable region between the binodal and spinodal curves and $A_{un}$ is the area of the unstable region under the spinodal curve. The $A_{meta}$ value is the sum of two contributions; the area of the water rich metastable region $A_{metaW}$ and the area of the alcohol rich metastable region $A_{metaA}$. Then the following relations: $A_{2Ph} = A_{meta} + A_{un}$ and $A_{meta} = A_{metaW} + A_{metaA}$ hold. Assuming $A_{1Ph} + A_{2Ph} = 1.00$, we obtain the following values for the most significant quantities:

As can be seen in the table the area of the two phase region increases significantly at increasing the chain length of the 1-alcohol: a very large increase is noted passing from 1-butanol to 1-pentanol (in this case the area $A_{2Ph}$ almost doubles), while the variation is smaller passing from 1-pentanol to 1-hexanol. All the sub-area of the two phase region increase as the alcohol hydrophobicity is enhanced but the unstable region shows the largest variation; as a consequence the ratio $A_{un}/A_{2Ph}$
increases on \( n \) as reported in the last column of the table. Even if the variation on \( n \) of the quantities reported in the table is clear and reasonable, it is not easy to predict which will be the behavior of the systems containing alcohols with longer hydrophobic chain. In fact the binary binodal and spinodal points, calculated by the NRTL coefficients present in the literature [24], show a peculiar trends. These values are reported in Figure 10 for the water rich side, the left branch of the binodal and spinodal curves, and in Figure 11 for the alcohol rich side, the right branch of the binodal and spinodal curves; the curves reported in Figures 10 and 11 do not have physical significance but are only a guide for eye.

In Figure 10 it is easily to see how the solubility in water of the alcohols with long hydrophobic chain approaches zero; at the same time also the spinodal points approach the composition limit \( x = -0.5773 \) that corresponds to pure water. It is therefore reasonable to predict for \( n \geq 8 \) a further decrease of \( A_{\text{metaW}} \) in line with the behavior observed for \( n = 4,5,6 \). Regarding the right branches of binodal and spinodal, it seems that the solubility of water in the 1-alcohols decreases for the first terms of the series and then it increases for \( n \geq 8 \). This implies that \( x_{bR} \), for \( n \geq 8 \), moves to smaller values; at the same time a decrease of the \( x_{sR} \) is also observed.
Table 1

Relative areas of some regions of interest for the ternary systems water – 1-butanol – 1-propanol, water – 1-pentanol – 1-propanol, water – 1-hexanol – 1-propanol.

<table>
<thead>
<tr>
<th>HOC₄, n = 4</th>
<th>A_{2Ph}</th>
<th>A_{metaW}</th>
<th>A_{un}</th>
<th>A_{metaA}</th>
<th>A_{un} / A_{2Ph}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.12</td>
<td>0.006</td>
<td>0.06</td>
<td>0.06</td>
<td>0.50</td>
</tr>
<tr>
<td>HOC₅, n = 5</td>
<td>0.23</td>
<td>0.007</td>
<td>0.14</td>
<td>0.08₅</td>
<td>0.61</td>
</tr>
<tr>
<td>HOC₆, n = 6</td>
<td>0.28</td>
<td>0.008</td>
<td>0.18</td>
<td>0.09₅</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Even if these data are probably affected by errors they could suggest a decrease of the two phase area not easily understandable. In this condition it is not easy to predict the values of the individual areas $A_{un}$, $A_{meta}$, $A_{metaW}$, and $A_{metaW}$.

The analysis of the LLE data for the systems water – 1-octanol – 1-propanol and water – 1-nonanol – 1-propanol and water – 1-butanol – 1-decanol will be undertaken in the near future to clarify this last aspect and to verify their potential as “solvent extractor” of 1-propanol by its aqueous solutions.

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REFERENCES

10. C. Stoicescu, O. Iulian and R. Isopescu, Liquid-Liquid Phase Equilibria of 1-Propanol + Water...


