

ON THE DETERMINATION OF THE SPINODAL CURVE FOR THE
SYSTEM WATER + CHLOROFORM + ACETIC ACID FROM THE
MUTUAL DIFFUSION COEFFICIENTS

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The four mutual diffusion coefficients have been determined for two sets of homogeneous compositions of the water + chloroform + acetic acid system at 25°C. By extrapolating the values of the diffusion coefficients determinant in the supersaturated region, we determined the spinodal compositions for two sets of experiments. The comparison between the experimental results and the theoretical prediction of the spinodal curve within an extended Wheeler-Widom model shows an excellent agreement.

Key words: ternary system; amphiphilic solvent; binodal and spinodal curves; molecular lattice model; Ising model; mutual diffusion coefficients.

INTRODUCTION

Water (component 1) and chloroform (component 2) are both liquids at 25° and are almost completely immiscible. So shaking together some water and some chloroform, two phases are obtained; an aqueous phase containing traces of chloroform and a chloroform phase containing traces of water. Adding acetic acid (component 3) to this heterogeneous system and shaking again we observe that the mutual solubility of water and chloroform increases: the aqueous phase contains a larger quantity of chloroform and the chloroform phase contains a larger amount of water. The compositions of the two phases in chemical equilibrium are called “binodal compositions” and the segment that joints these two compositions is indicated as “tie line”. All the couple of binodal compositions obtained for different amount of added

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acetic acid form the “binodal curve”; on this curve the “plait point”, indicated as P, is defined as the point at which the binodal compositions are identical. We note also that the amount of acetic acid is not the same in the two phases; in the triangular phase diagram this fact translates into an asymmetric binodal curves and in tie-lines that are not parallel to the side corresponding to the binary water-chloroform system. At increasing acetic acid concentration the system tends to become homogeneous with a single phase containing all the components. A similar behavior is observed adding ethanol to a water – chloroform biphasic system [1–4].

This behavior can be easily explained considering that both acetic acid and ethanol behave as amphiphilic solvent in respect to water and chloroform. In fact their molecules have a hydrophilic moiety, respectively the carboxylic group, $-\text{COOH}$, and the alcoholic one, $-\text{OH}$, and a hydrophobic one, the CH_3- and the CH_3CH_2- one. Therefore the same amphiphilic molecule can interact with water, through the hydrophilic moiety, and with chloroform, through the hydrophobic one. As a consequence the mutual solubility of water and chloroform increases.

A simple model of a ternary system containing two immiscible components and an amphiphilic solvent for both of them is due to Wheeler and Widom [5]. They considered three different bifunctional (rodlike) molecules, AA and BB, for the two immiscible liquids, and AB, for the amphiphilic solvent. These molecules cover completely the bonds of a regular lattice (one molecule per bond) in such a way that only A or only B ends may meet at a given lattice site. To account for the complete insolubility of the pure AA and BB phases, there is an infinite repulsion between A and B molecular ends associated to the same site. If all the other interactions are neglected, the Wheeler and Widom model reduces to the standard Ising model on the same lattice [5]. The original model was extended to the case of both two- [6] and three-body interactions [7–8] between the molecular ends associated to the same lattice site. This extended Wheeler-Widom model allows to predict asymmetric binodal curves in the triangular phase diagram of the ternary system and therefore can be applied to amphiphilic systems as water + chloroform + acetic acid.

The description of a phase diagram is generally given by the binodal and spinodal curves. The binodal curve, as defined before, divides the homogeneous monophasic region from the two-phase region. In this two-phase region the spinodal curve divides the metastable from the unstable region. For compositions between the binodal and spinodal we may have a supersaturation effect: although the solution is thermodynamically unstable, at small perturbations it remains mixed. On the contrary, under the spinodal curve all solutions will always spontaneously separate in two phases. The spinodal curve touches the binodal at the plait point. It is important to remark that while the binodal curve can be easily determined, the spinodal compositions can not be directly measured except for the plait point.

Because the determinant $\|D_{ij}\|$ of the matrix of the diffusion coefficients must be zero on the spinodal curve (see below) in 1978 it was suggested, from

some of us, that this condition could be used to obtain the spinodal compositions by extrapolating to zero the $\|D_{ij}\|$ values determined in the homogeneous region of the system [9]. In the same paper it was experimentally verified that the $\|D_{ij}\|$ values, determined for the ternary system water + chloroform + acetic acid at 25°C at five concentrations, see Fig. 1a, extrapolate to zero at the plait point. Two years later [10] the spinodal compositions of the binary system water-triethylamine have been determined at two different temperatures, 19°C and 20°C.

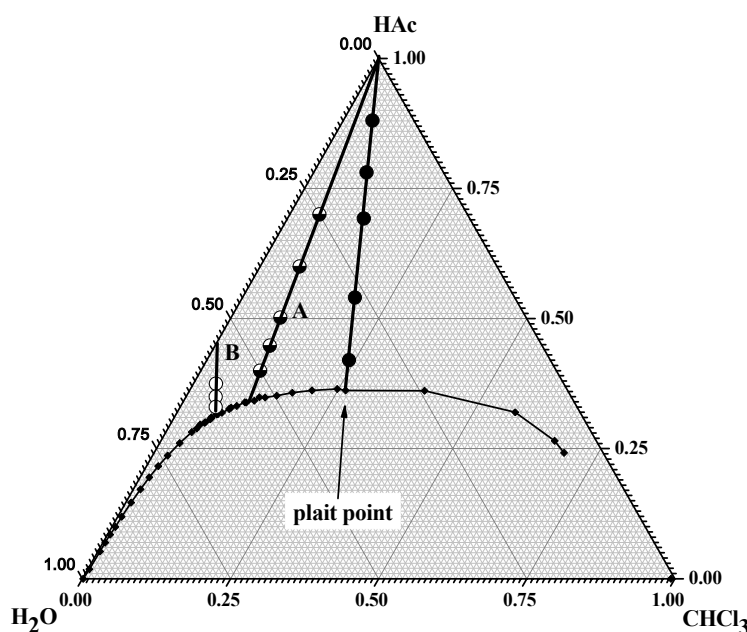


Fig. 1a –Triangular diagram in mole fraction. ● reference 10; set A: $X_2 = 0.2004X_1$, reference 12; set B: $X_2 = -0.5517 + 1.0028X_1$, this paper

In a previous work [11] we have performed mutual diffusion experiments at other compositions of the same ternary system, with a fixed different water/chloroform mole ratio, set A in Fig. 1a, with the aim to analyze the possibility to obtain reliable spinodal compositions. Very recently, this extrapolation procedure has been compared with the theoretical spinodal curve predicted by the modified Wheeler and Widom model described in more details below. As shown in Fig. 2, the theoretical spinodal curve is in very good agreement with the spinodal composition obtained by extrapolating to zero the $\|D_{ij}\|$ values.

The aim of the present work is to verify this extrapolation procedure by performing another set of diffusion experiments in a different region of the phase

diagram and closer to the binodal curve. Due to the high volatility of chloroform, we preferred not to work in the region of high chloroform mole fraction, on the right side of the ternary phase diagram, and also to avoid solutions with very low amount of chloroform. The compositions at which we measured the diffusion coefficients are indicated in Fig. 1a and Fig. 1b as the set B of points.

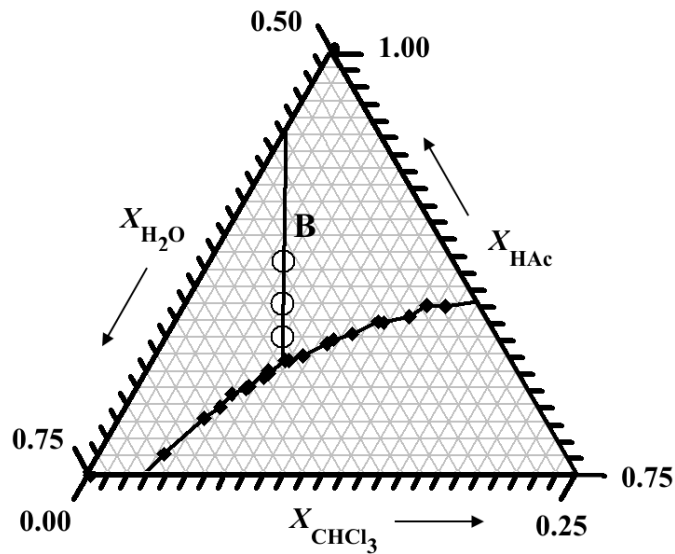


Fig. 1b – Detail of Figure 1a; set B.

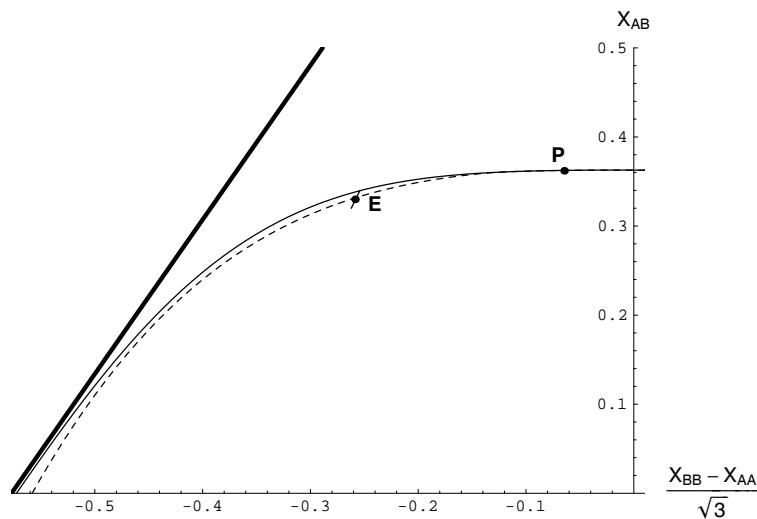


Fig. 2 –The theoretical spinodal curve (*dashed line*) and the experimental binodal curve (*continuous line*). The spinodal composition obtained by extrapolation of the experimental $\|D_{ij}\|$, set A, is represented by a circle with error bar and denoted by E.

THEORETICAL ASPECTS AND RESULTS

THEORETICAL SPINODAL

In determining the theoretical spinodal curve for the system water + chloroform + acetic acid at 25°C, we used the extended Wheeler-Widom model on the honeycomb lattice with three-body interactions between the molecular ends associated to the same lattice site [7,12]. Based on the equivalence between the molecular model and the standard Ising model (spin $\frac{1}{2}$, nearest neighbor interactions only) on the same honeycomb lattice, where the ferromagnetic transition, corresponding to the phase separation in the molecular model, is known (both analytically and in various approximations), we tried to get the best theoretical binodal curve that fit properly the experimental points. As explained in the Ref. [12], this can be done only in the mean-field approximation of the corresponding Ising model and only locally (*i.e.*, a global fit fails). For each of the experimental binodal point and its associated tie line, we constructed within our model the corresponding spinodal point. A global theoretical spinodal curve for the system can be thus determined. The results are presented in Fig. 2.

DIFFUSION

Mutual diffusion experiments are usually performed stratifying, in a suitable cell, two solutions at different composition and then following the time evolution of the “diffusion” boundary. The use of this technique is obviously limited to the homogeneous region of the system. For details on the theory of diffusion and on the experimental techniques, we remand the reader to the huge literature present in this field [14,15].

In a ternary system the Fick’s laws describe, by a phenomenological point of view, the flow of solute i , in terms of four mutual diffusion coefficients D_{ij} and in terms of the solute concentration gradients ∇C_i .

$$\begin{cases} -J_1 = D_{11} \left(\frac{\partial c_1}{\partial x} \right) + D_{12} \left(\frac{\partial c_2}{\partial x} \right) \\ -J_2 = D_{21} \left(\frac{\partial c_1}{\partial x} \right) + D_{22} \left(\frac{\partial c_2}{\partial x} \right) \end{cases} \quad (1)$$

The main diffusion coefficients, D_{ii} , are independent on the concentration scale used, while the cross diffusion coefficients, D_{ij} , do depend on this choice [16].

However in non-equilibrium thermodynamic the real driving force of the diffusion process is the gradient of the chemical potential [17], and the following relation holds between the matrix of the experimental diffusion coefficients, the matrix of the thermodynamic diffusion coefficients, often reported as mobility, and the matrix of the derivatives of the chemical potential

$$\begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix} = \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \times \begin{bmatrix} \mu_{11} & \mu_{12} \\ \mu_{21} & \mu_{22} \end{bmatrix} \quad (2)$$

where the μ_{ij} are defined as

$$\mu_{ij} = \left(\frac{\partial \mu_i}{\partial c_j} \right)_{c_i} \quad (3)$$

At any spinodal composition the determinant of the derivative of the chemical potentials must be zero by definition and therefore also the determinant of the experimental diffusion coefficients must be zero, $\|D_{ij}\| = 0$, independently by the scale of concentration used [10,16].

As said above, we performed two different sets of diffusion experiments to investigate two different portions of the spinodal curve. In the first set, set A, the diffusion coefficients have been determined at five compositions of the system having a fixed ratio between the water and chloroform mole fraction [12]: this means that all the compositions are aligned on a segment that starts from the corner of the diagram phase triangle that corresponds to pure acetic acid. The equation that links the chloroform and water mole fraction is:

$$X_2 = 0.2004 X_1$$

The individual diffusion coefficients and the values of $\|D_{ij}\|$ are reported, for these five compositions, in Table 1.

The second set of experiments, set B, has been done at three different compositions. With the aim to get closer to the binodal curve, we preferred not to fix the ratio between the water and the chloroform mole fraction. The relation between the X_1 and X_2 is the following:

$$X_2 = -0.5517 + 1.0028 X_1$$

The results are reported in Table 2.

The spinodal composition corresponding to each set of experiments has been calculated as the intersection point between the theoretical spinodal curve and the straight A- or B-line. The two spinodal compositions are respectively:

$$\text{set A} \quad X_1 = 0.558; X_2 = 0.112; X_3 = 0.332$$

$$\text{set B} \quad X_1 = 0.621; X_2 = 0.071; X_3 = 0.308$$

We expect that for these two compositions the determinant of the matrix of the mutual diffusion coefficients should be zero. In other words, if there is a good agreement between the theory and experiment, the positions of these spinodal points should be consistent with the experimental $\|D_{ij}\|$ values from Tables 1 and 2.

Table 1

Set A. Experimental diffusion coefficients and $\|D_{ij}\|$ values at the five homogeneous compositions and at the theoretical spinodal composition corresponding to $X_2 = 0.2004X_1$

X_1	X_2	D_{11} $10^9 \text{ m}^2 \text{ s}^{-1}$	D_{12} $10^9 \text{ m}^2 \text{ s}^{-1}$	D_{21} $10^9 \text{ m}^2 \text{ s}^{-1}$	D_{22} $10^9 \text{ m}^2 \text{ s}^{-1}$	$\ D_{ij}\ $ $10^{18} \text{ m}^4 \text{ s}^{-2}$
0.2499	0.0503	0.685 ± 0.0690	0.394 ± 0.0790	0.107 ± 0.0210	0.753 ± 0.0750	0.483 ± 0.0760
0.3333	0.0667	0.632 ± 0.0630	0.451 ± 0.0900	0.138 ± 0.0280	0.811 ± 0.0810	0.439 ± 0.0720
0.4150	0.0830	0.564 ± 0.0560	0.403 ± 0.0810	0.185 ± 0.0370	0.728 ± 0.0730	0.312 ± 0.0560
0.4597	0.0925	0.386 ± 0.0390	0.540 ± 0.0890	0.117 ± 0.0230	0.699 ± 0.0700	0.222 ± 0.0450
0.5000	0.1000	0.406 ± 0.0410	0.461 ± 0.0920	0.181 ± 0.0360	0.544 ± 0.0540	0.139 ± 0.0450
0.558	0.112	–	–	–	–	0.000

Table 2

Set B. Experimental diffusion coefficients and $\|D_{ij}\|$ values at the three homogeneous compositions and at the theoretical spinodal composition corresponding to $X_2 = -0.5517 + 1.0028X_1$.

X_1	X_2	D_{11} $10^9 \text{ m}^2 \text{ s}^{-1}$	D_{12} $10^9 \text{ m}^2 \text{ s}^{-1}$	D_{21} $10^9 \text{ m}^2 \text{ s}^{-1}$	D_{22} $10^9 \text{ m}^2 \text{ s}^{-1}$	$\ D_{ij}\ $ $10^{18} \text{ m}^4 \text{ s}^{-2}$
0.5879	0.0383	0.421 ± 0.0260	0.788 ± 0.1310	0.060 ± 0.0090	0.635 ± 0.0260	0.220 ± 0.0530
0.6003	0.0507	0.492 ± 0.0140	0.604 ± 0.0390	0.110 ± 0.0070	0.500 ± 0.0150	0.180 ± 0.0180
0.6100	0.0600	0.349 ± 0.0680	0.571 ± 0.1550	0.088 ± 0.0280	0.448 ± 0.0580	0.106 ± 0.0510
0.621	0.071	–	–	–	–	0.000

DISCUSSION AND CONCLUSION

In Fig. 3 we report the experimental $\|D_{ij}\|$ values as function of the acetic acid mole fraction for both sets A and B (empty symbols): the corresponding spinodal values determined as explained above are also shown (solid symbols). As can be seen from Fig. 3, the spinodal compositions are, in both cases, in good agreement with the trend of the experimental $\|D_{ij}\|$ values decreasing to zero. This agreement is checked quantitatively below.

In Ref. [12] we fitted, for the set A, a second degree polynomial to the five experimental $\|D_{ij}\|$ data (solid line in Fig. 3). By extrapolating this curve (dotted

line in Fig. 3) we obtained that the value of the acetic acid mole fraction that corresponds to $\|D_{ij}\|=0$ is equal to $X_3 = 0.33 \pm 0.01$ in excellent accord with the above computed spinodal composition, $X_3 = 0.332$.

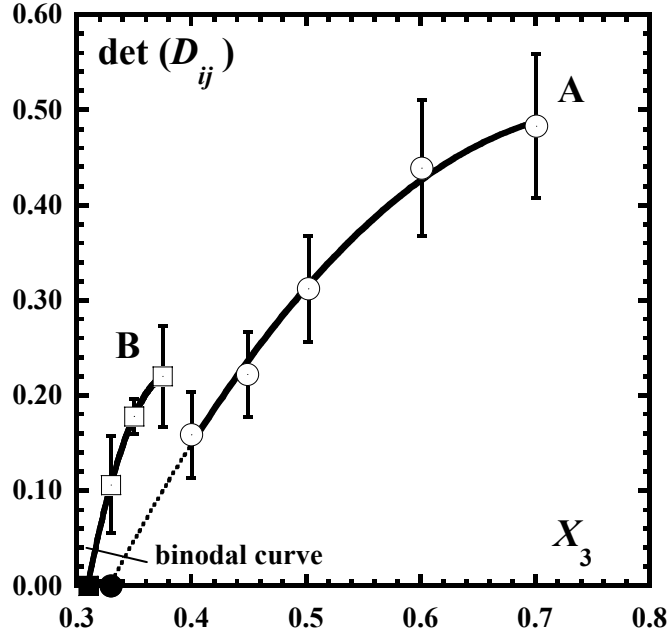


Fig. 3 – $\|D_{ij}\|$ experimental values as a function of X_3 . \circ set A ($X_2 = 0.2004X_1$); \square set B

$X_2 = -0.5517 + 1.0028X_1$. $\|D_{ij}\|$ values corresponding to the spinodal composition: \bullet set A; \blacksquare set B.

The three experimental points corresponding to the set B are not enough to perform a similar fitting procedure. Nevertheless, in order to check how good is the agreement between the experimental $(X_3, \|D_{ij}\|)_B$ data and the predicted spinodal point $(X_3, 0)_B$, we considered all the data together and we fitted a second degree polynomial to these four “heterogeneous data” (solid line in Fig. 3). The fitting equation is:

$$\|D_{ij}\| = (-5.9 \pm 0.5) + (31 \pm 3) \cdot X_3 + (-42 \pm 4) X_3^2$$

with $\chi^2 = 3.3 \cdot 10^{-5}$ and $R = 0.99951$. The small errors of the polynomial coefficients and the values of χ^2 and R indicate a very good agreement between the experimental data and the spinodal composition predicted by the modified Wheeler and Widom model.

Based on these results we can reasonably claim that, in general, the experimental diffusion coefficients measured in the homogeneous region can be used to estimate the position of the spinodal curve that separates the metastable region from the unstable one in the phase diagram of the system. However, we expect this extrapolation procedure might be less confident for systems where the resulting spinodal curve is well separated from the binodal one, *i.e.*, systems with a large metastable region.

According to our results, the trend of $\|D_{ij}\|$ vs. X_3 towards the spinodal curve is not affected by crossing the binodal curve; the same behavior can be assumed in our opinion to the individual D_{ij} diffusion coefficients. Knowing the diffusion coefficients in the supersaturated region would allow in principle the study the time evolution of the system in this regime.

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