Spinodal Composition of the System
Water + Chloroform + Acetic Acid at 25 °C

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Abstract A theoretical spinodal curve for the system water + chloroform + acetic acid at 25 °C is derived using a lattice model for ternary amphiphilic solutions: rod-like molecules covering the bonds of the honeycomb lattice with three-body interactions between the molecular ends associated to the same lattice site. The molecular model is equivalent to the standard Ising model on the same lattice; its mean-field solution is the most appropriate for reproducing, by local fitting, the experimental data for the binodal composition. The derived spinodal curve is in very good agreement with the spinodal composition determined also in the present work from the measured diffusion coefficients recently reported for the same system.

Keywords Ternary amphiphilic solution · Spinodal curve · Molecular lattice model · Ising model

1 Introduction

In a previous paper [1] we reported the values of the diffusion coefficients determined at five compositions of the system water + chloroform + acetic acid at 25 °C. The system presents
a large solubility gap due to the almost complete insolubility of water and chloroform. The binodal (coexistence) curve and the tie lines of this system have been known for a long time [2]. We showed in Ref. [1] that in approaching the binodal curve by decreasing the amount of the acetic acid at constant mole ratio of water and chloroform, the main diffusion coefficients decrease whereas the cross-diffusion coefficients increase. A similar behavior was remarked in approaching the plait point of the same system [3]; in that work it was also shown that the determinant of the diffusion coefficients tends to zero at the plait point, confirming thus the theoretical prediction that the spinodal and binodal curves meet at this point. From the diffusion coefficients reported in Ref. [1] we can extract, as we show in this paper, information about a spinodal point different from the plait point.

The main aim of the present work is to derive a theoretical spinodal curve that could be relevant to the water + chloroform + acetic acid system. We will do this by using an extension of the lattice model introduced many years ago by Wheeler and Widom to describe the phase transitions in ternary amphiphilic systems [4], such as water and chloroform, in the presence of a solvent for both solutes (for example, ethanol or acetic acid). The immiscibility of water and chloroform translates in the Wheeler-Widom model to infinite repulsions between the molecules of the solutes. The extended model used in the present work considers finite three-body molecular interactions on the honeycomb lattice [5, 6] and can be thus more appropriate to describe realistic systems. A simplified version of this extended model, considering only two-body interactions between the molecules, was previously used to show how the spinodal curve can be derived within the mean-field and Bethe approximations [7].

The paper is organized as follows. In Sect. 2 we recall the results reported in Ref. [1] for the four diffusion coefficients of the system water + chloroform + acetic acid at 25 °C and, from the determinant of the diffusion coefficients, we will find by extrapolation the corresponding spinodal composition. Section 3 is devoted to a short review of the extended Wheeler-Widom model used in deriving our results. As we show in Sect. 4, even if the model admits an exact solution for the binodal curve, we have to restrict our considerations to the mean-field approximation for the equivalent Ising model. In order to determine a theoretical spinodal curve for the system that can be compared with the experimental data, good agreement between the theory and experiment for the binodal curve is crucial. In Sect. 5 we show the theoretical binodals generated by our model can reproduce the mutual solubility data for the system, by adjusting the model parameters, only in small ranges of binodal compositions, i.e., a global fit fails. The problem can be handled by fitting the data with local binodals and we will show in the same section how a global spinodal curve can be determined. The spinodal composition obtained from the diffusion experiments is in very good agreement with our predicted spinodal curve. The last section summarizes the results of the work.

2 Experimental Determination of the Spinodal Composition

In Ref. [1] we have presented the mutual diffusion coefficients at five compositions in the homogeneous region of the system water (component 1) + chloroform (component 2) + acetic acid (component 3). In the same reference we mentioned also the possibility of obtaining the spinodal compositions from the knowledge of the diffusion coefficients $D_{ij}$ ($i, j = 1, 2$) measured in the homogeneous region of the system.

The four experimental coefficients $D_{ij}$ that define the mutual diffusion in a ternary system, solute 1 + solute 2 + solvent 3, are related to the derivatives of the solute chemical