

# **The understanding of the three-dimensional graphical behavior of the L-L-S phase equilibrium as a valuable tool to avoid spurious or incoherent experimental data**

M.M. Olaya, J.A. Labarta\*, A. Gómez and A. Marcilla

*Dpto. Ingeniería Química, Universidad de Alicante, Apdo. 99, Alicante 03080, Spain.*

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## **Abstract**

The complexity and variety of possible behaviors of the quaternary liquid-liquid, liquid-liquid-solid equilibrium at constant temperature are very high and, sometimes, are not well understood. It is not difficult to find references in literature where important misinterpretations and mistakes are committed as a consequence of applying a non-adequate experimental methodology and a lack of the spatial point of view. Thus, the objective of the present paper is to show several examples where special behaviors are selected to clarify some aspects concerning the experimental determination and graphical representation of liquid-liquid-solid equilibrium data, and emphasize the importance of the knowledge and consideration of the qualitative expected behavior of the system under study, obtained from the binaries.

*Keywords:* Graphical representations; Liquid-liquid and Solid-fluid equilibria.

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## **Introduction**

In a previous paper [1] some of the problems associated with a non-correct methodology to obtain liquid-liquid-solid equilibrium data in quaternary systems was presented. Later, a methodology, to study this type of systems, was proposed and applied to the water + ethanol + 1-butanol + sodium chloride systems at 25°C [2]. Other systems have been studied using this systematic method yielding good results [3] [4] [5]. However, there is still part of the recent

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\* Author to whom all correspondence should be addressed. Tel.: (34) 965 903 789. Fax: (34) 965 903 826. E-mail: [ja.labarta@ua.es](mailto:ja.labarta@ua.es)

literature that treats these topics showing misinterpretations and mistakes as a consequence of applying a non-adequate experimental methodology and a lack of the spatial point of view, both leading to incomplete and even spurious sets of data. As J.S. Marsch [6] said: “erroneous diagrams have appeared because the constructor failed to observe the rules of construction”:

Other comments merit the frequent practice in quaternary liquid-liquid or liquid-liquid-solid equilibria to group two components as a pseudo component (for instance, [7] and [8]). This practice, although not intrinsically erroneous (this methodology is correctly applied for example in paper [7]), is inadvisable since it does not clarify the behavior of the system and frequently leads to misinterpretations. Papers [8], [9], [10] and [11] are some examples where incorrect equilibrium data are presented because the treatment of the systems as pseudo ternary systems is not applied with the necessary care. On the contrary, the systematic study of all the equilibrium regions applying any correct methodology based on the consideration of the system as a quaternary system as, for instance, that suggested in [2] [3] [4] and [5], is strongly recommended.

The presentation of three-dimensional qualitative figures of the equilibrium behavior of the systems under study must be done with care, showing all the equilibrium regions, with suitable or feasible shapes and behavior, thus avoiding misinterpretation. In other cases, the objective of such figures, which is to help the understanding of the behavior of the system, is hardly fulfilled and may even produce a contrary effect.

The complexity and variety of possible behaviors of the quaternary liquid-liquid, liquid-liquid-solid equilibrium at constant temperature are very high. Thus, instead of trying to be extensive in the description of this paper, we will try to show several examples where some selected behaviors are explained in detail, providing different projections as well as the three-dimensional qualitative representations of the different surfaces and boundaries of the system, in order to emphasize the importance of such qualitative knowledge of the behavior of the

system, which is expected from the behavior of the corresponding binaries, and which is highly helpful in selecting the experimental methodology for equilibrium data determination.

The purpose of this paper is to clarify some aspects concerning the experimental determination and graphical representation of liquid-liquid-solid equilibrium data and emphasize the importance of the knowledge and consideration of the qualitative expected behavior of the system under study, obtained from the binaries and ternaries. Unfortunately, this suggestion is frequently obviated.

### **Liquid-liquid-solid equilibrium**

Two different cases are presented, both quaternary systems with only one pair of liquids partially miscible, but one of them with one salt and the other with two different salts.

Example 1: Water + Solute + Solvent + Salt (water + solute and solute + solvent are miscible in all proportions and water + solvent are partially miscible).

These systems are quaternary systems, and therefore, for the representation of the equilibrium data, a three-dimensional representation must be used. For instance, a regular tetrahedron can be used. The liquid-liquid-solid phase equilibrium diagram for these systems can be very different depending on the nature of the components and the temperature. For example, Figure 1a shows the qualitative representation of a quaternary such as water + ethanol + 1-butanol + NaCl at 25°C, showing all equilibrium regions of the system: 1L, 2L, 1L+1S and 2L+1S. Figure 1b corresponds to a system where a two-liquid equilibrium region appears in the ternary water + solute + salt, although water and solute are totally miscible (for example water + acetone + 1-butanol + NaCl at 25°C).

Many authors consider these types of systems as pseudo ternary systems, grouping water + salt in a single component, and working on a salt-free basis. If the quaternary diagram is considered, this methodology of work involves preparing initial mixtures in sectional planes

of the tetrahedron with constant water/salt ratios (Figure 2a). This consideration does not imply a mistake by itself if:

- (1) All the components, including the salt, are analyzed in all equilibrium phases
- (2) The quaternary behavior of the systems is considered.

However, in some papers, these considerations have not been taken into account, and therefore mistakes have been committed and misinterpretations can be generated.

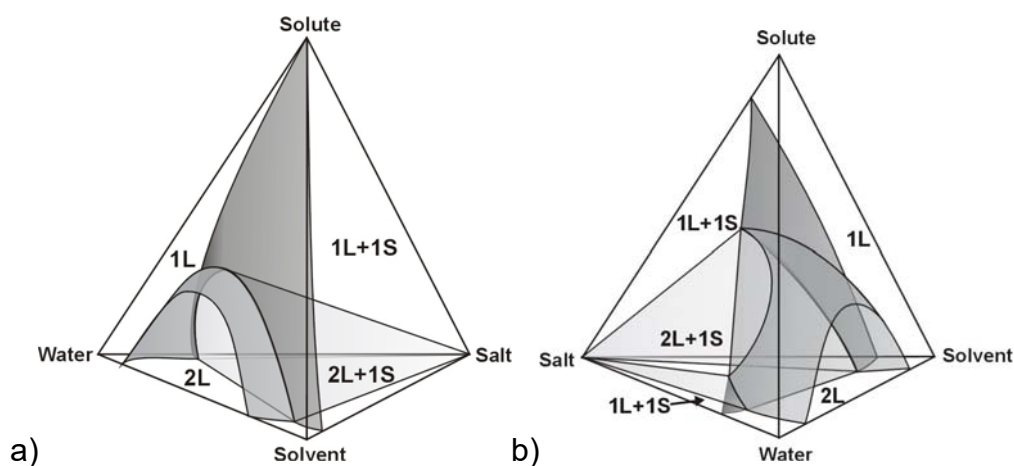


Figure 1. Qualitative representation of the equilibrium of the a) Water-Ethanol-1-Butanol-Sodium chloride and b) Water-Acetone-1-Butanol-Sodium chloride systems at 25°C.

For example, concerning the case (1), in some papers ([8], [9], [10] and [11]) the salt has not been analyzed in the equilibrium phases. Therefore, it is not clear if the salt only concentrates in the aqueous phase or if the distribution of salt is the same in the organic and aqueous phases, and assumes, therefore, that the tie-lines obtained are placed on the same sectional plane of the quaternary equilibrium diagram where the initial mixtures were prepared. As can be observed in Figure 2b, the tie lines obtained (straight lines connecting equilibrium points on curve C in the figure) when initial mixtures are prepared in sectional pseudo ternary planes, are not placed on this sectional plane. On this sectional plane, where the initial mixtures were prepared, another solubility curve (C') exists, corresponding to the intersection between the sectional plane and the quaternary solubility surface, but this curve C' does not contain tie lines of the system, and cannot be confused with C.

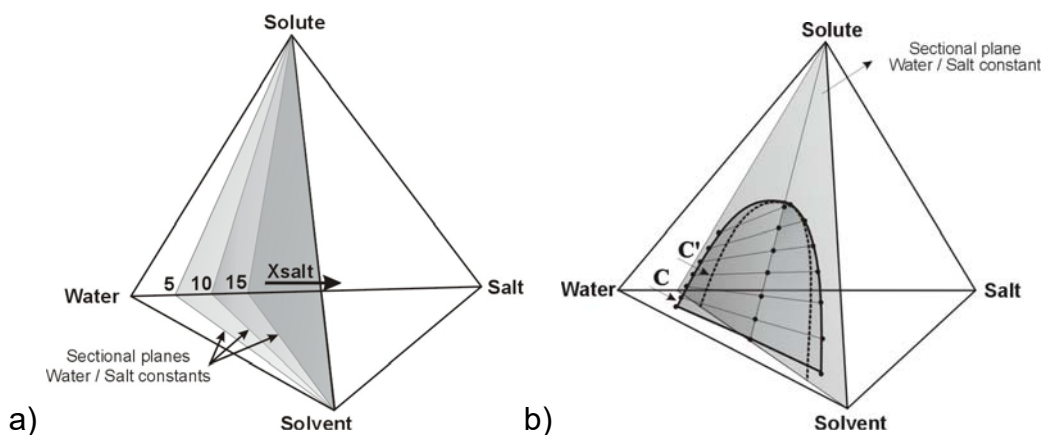


Figure 2. a) Sectional plane of the regular tetrahedron shown in Figure 1a), with constant water/salt ratios. b) Tie lines obtained for initial mixtures belong to such a sectional plane.

Furthermore, the representation of quaternary systems as those considered in the present example, using two-dimensional pseudo ternary diagrams (triangles) does not provide clear information about the system's global behavior. Usually, three-dimensional figures, such as Figures 1a and 1b, for quaternary systems including salts are not presented.

On the other hand, another different type of problem can appear if case (2) is not considered that is to say, if the quaternary behaviour of the system is obviated. When authors, who treat these systems as pseudo ternary ones, select the ratios water/salt constant to obtain tie-lines in the two-liquid regions, they choose those ratios where salt is soluble in water (for example 5, 10, 15... per cent of salt in water, until saturation). In this way, they look for and report sections of the quaternary diagram as that shown in Figure 3. But, other complex intersections of the system (Figures 4, 5 and 6) can happen, which the authors are probably not aware of as a consequence of not studying the three-dimensional representations as those shown in these papers. This means that the study of the system cannot be adequately planned and that incomplete figures, and therefore incorrect diagrams, are presented.

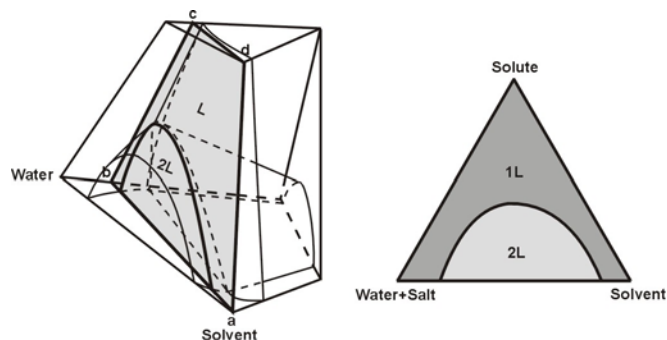


Figure 3. Intersection between a sectional plane with constant water/salt ratio and the solubility surfaces leading to a pseudo ternary system of type 1.

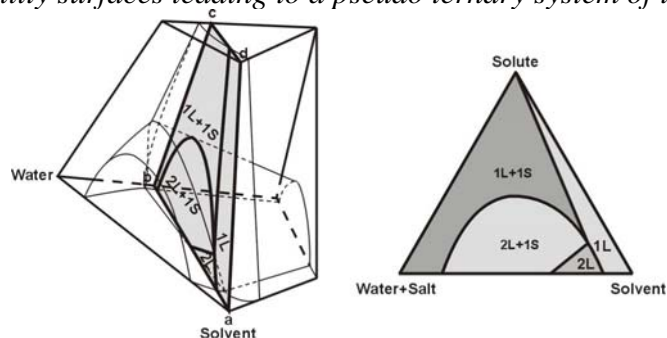


Figure 4. Intersection between a sectional plane with constant water/salt ratio and the solubility surfaces leading to a complex pseudo ternary system with four different zones.

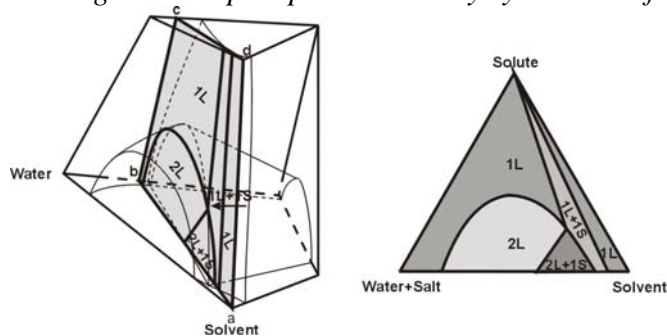


Figure 5. Intersection between a sectional plane with constant water/salt ratio and the solubility surfaces leading to a complex pseudo ternary system with five different zones.

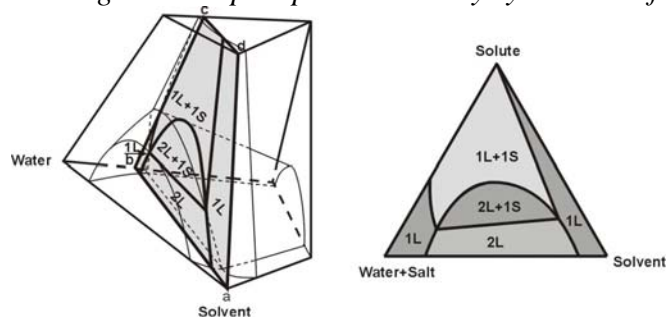


Figure 6. Intersection between a sectional plane with constant water/salt ratio and the solubility surfaces leading to a complex pseudoternary system with five different zones.

### Example 2: Water + Solvent + Fatty acid (A) + Fatty acid (B)

In this example we consider a quaternary system with two liquid components (water and solvent) totally miscible and two different fatty acids (A and B), which lead to two liquids in equilibrium appearing. In paper [12], the importance of the study of the equilibrium data in ternary and quaternary systems including fatty acids, included in a large number of biochemical products, is commented on. These authors study ternary systems including water + ethanol or acetone + fatty acid (lauric acid or myristic acid or palmitic acid). From animal and vegetable sources, mixtures of fatty acids are usually derived. Therefore, the interest of studying systems as those presented in paper [12] but including more than one fatty acid (for instance two fatty acids) is obvious.

The quaternary systems composed of water + solvent + fatty acid (A) + fatty acid (B) at a constant temperature and pressure, must present an equilibrium diagram like that we have represented in Figure 7 (qualitative representation of the complete diagram) and Figure 8 (which has been drawn in order to facilitate the understanding of Figure 7, and where the different equilibrium regions have been taken out step by step). In these figures all equilibrium regions of these types of systems can be clearly observed, i.e. the 1L, 1L+1S(A), 1L+1S(B), 1L+2S(A and B), 2L, 2L+1S(A), 2L+1S(B) and 2L+2S (A and B). The existence of many of these equilibrium regions would probably be obviated if these type of systems were studied as pseudoternary systems and, in any case, the information provided could be not so complete as when considering their quaternary nature.

The three-dimensional representation of the quaternary systems has to be considered when the equilibrium data are going to be obtained. Not considering the third dimension may give rise to erroneous conclusions.

## Conclusions

The present paper shows some examples where special behaviours are selected to help the understanding of the shapes and the behaviour of the systems, and to clarify some aspects concerning the experimental determination and graphical representation of liquid-liquid-solid equilibrium data, and also emphasise the importance of the knowledge and consideration of the expected qualitative behaviour of the system under study, obtained from the binaries and ternaries data, in order to avoid misinterpretations and mistakes as a consequence of applying a non-adequate experimental methodology and finally to determinate the boundary surfaces that divide the different zones with the same number of phases in the phase equilibria diagrams.

## References

- [1] F. Ruiz Beviá and A.F. Marcilla Gomis, *Fluid Phase Equilibria*, 89 (1993) 387-395.
- [2] Marcilla, A., Ruiz, F. and Olaya, M.M., *Fluid Phase Equilibria*, 105 (1995) 71-91.
- [3] Marcilla, A., Ruiz, F. and García, A.N., *Fluid Phase Equilibria*, 112, (1995) 273-289.
- [4] Olaya, M.M, García, A.N., and Marcilla, A., *J. Chem. Eng. Data*, 41 (1996) 910-917.
- [5] Olaya, M.M., Conesa, J.A., and Marcilla, A., *J. Chem Eng. Data*, 42, 5 (1997) 858-864.
- [6] J.S. Marsch, *Principles of Phase Diagrams (Alloys of Iron Research, Monograph Series)*, First Edition, McGraw-Hill Book Company, Inc., New York, 1935.
- [7] Sólamo, Horacio N., Bonatti, Carlos M., Zurita, José L., Gramajo de Doz, Mónica B., *Fluid Phase Equilibria*, 137 (1997) 163-172
- [8] Sharma, S., Pandya, G., Chakrabarti, T., Khanna, P., *J. Chem. Eng. Data*, 41 (1996) 306-309.
- [9] Saravanan, G., and Srinivasan, D., *J. Chem. Eng. Data*, 30 (1985) 166-171.



[10] Rajendram, M., Renganarayanan, S., Srinivasan, D., Fluid Phase Equilibria, 70 (1991) 65-106

[11] Rajendram, M., and Srinivasan, D., Fluid Phase Equilibria, 44 (1988) 53-75.

[12] Maeda, K., Satoshi, Y., and Hirota, S., Fluid Phase Equilibria, 130 (1997) 281-294.

### *Updated references*

1. Marcilla A, Reyes-Labarta JA, Olaya MM. Should we trust all the published LLE correlation parameters in phase equilibria? Necessity of their Assessment Prior to Publication. Fluid Phase Equilib. 2017; 433: 243-252.
2. Reyes JA, Conesa JA, Marcilla A, Olaya MM. Solid-Liquid Equilibrium Thermodynamics: checking stability in multiphase systems using Gibbs Energy Function. Ind. Eng. Chem. Res. 2001; 40: 902-907.
3. Olaya MM, Marcilla A, Serrano MD, Botella A, Reyes-Labarta JA. Simultaneous correlation of LL, LS and LLS equilibrium data for water + organic solvent + salt ternary systems. anhydrous solid phase. Ind. Eng. Chem. Res. 2007; 46(21): 7030-7037.
4. Marcilla A, Reyes-Labarta JA, Olaya MM, Serrano MD. Simultaneous correlation of liquid-liquid, liquid-solid, and liquid-liquid-solid equilibrium data for water + organic solvent + salt ternary systems: hydrated solid phase formation. Ind. Eng. Chem. Res. 2008; 47: 2100-2108.

### *Figure Captions*

**Figure 1.** Qualitative representation of the equilibrium of the a) water-ethanol-1-butanol-sodium chloride and b) water-acetone-1-butanol-sodium chloride systems at 25°C.

**Figure 2.** a) Sectional plane of the regular tetrahedron shown in figure 1a), with constant water/salt ratios. b) Tie lines obtained for initial mixtures pertaining to such a sectional plane.

**Figure 3.** Intersection between a sectional plane with constant water/salt ratio and the solubility surfaces leading to a pseudoternary system of type 1.

**Figure 4.** Intersection between a sectional plane with constant water/salt ratio and the solubility surfaces leading to a complex pseudoternary system with four different zones.

**Figure 5.** Intersection between a sectional plane with constant water/salt ratio and the solubility surfaces leading to a complex pseudoternary system with five different zones.

**Figure 6.** Intersection between a sectional plane with constant water/salt ratio and the solubility surfaces leading to a complex pseudoternary system with five different zones.

**Figure 7.** Qualitative representation of the equilibrium of a water-solvent-fatty acid (A)-fatty acid (B) system.

**Figure 8.** Different regions in the qualitative representation of figure 7.