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Comments

Letter to the Editor: Phase Behavior in Liquid−Liquid−Solid Quaternary Systems

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Quaternary liquid−liquid equilibria involving solid components are receiving increasing attention, and several papers related to this topic have recently appeared in the *Journal of Chemical Engineering Data.* For instance, Sharma et al. (1996) and Escudero et al. (1996) present results for such systems. In these papers the authors treat two of the components as a single one, thus considering the system as pseudoternary. The concept of pseudocomponents (i.e., considering mixtures of two or more components as a single component in order to facilitate the study of multicomponent systems) is very old. The classic book *Liquid−Liquid Equilibrium* by Francis (1963) devotes a full chapter to this topic, showing some of the problems involved. This concept is valid when the two compounds are very similar in nature and their behavior is expected to be similar. This is not, obviously, the case of water and an inorganic salt or an organic salt. Ruiz et al. (1986) showed the marked influence of the presence of a propyl ether isomer on the liquid−liquid equilibria phase behavior of the system water + phosphoric acid + propyl ethers, which can cause the appearance of a third liquid phase. Clearly, this system cannot be considered in terms of a pseudoternary system.

In 1993 *Fluid Phase Equilibria* published a letter to the Editor (Ruiz and Marcilla, 1993) where we discussed some relevant aspects concerning the methodology for the study of the salting out effect in liquid−liquid equilibria and the problems involved with the assumption that any quaternary system can be treated as a pseudoternary by grouping two or more components (i.e. considering the group water + salt as a single component). In that work we stated how the problems in the assumptions made by various authors in quaternary systems involving one solid and three liquid components should be considered, studied, and analyzed. Recently, the *Journal of Chemical and Engineering Data* has published several papers where an adequate methodology was not applied and meaningless results are presented and discussed (i.e., Sharma et al., 1996, and Escudero et al., 1996). The objective of the present paper is to comment on the general problem of the phase behavior of four component systems.

Phase Behavior of Common Quaternary Salting out Systems

The phase behavior of four-component systems with phase separation can be very complicated. Nevertheless, the different equilibrium regions present in these systems can be qualitatively estimated from the behavior of the four ternaries involved. Obviously, the number of possible combinations can be very high, but the methodology to be applied can be very simple and systematic. Figures 1−3 show three possibilities: water + ethanol + 1-butanol + sodium chloride (Marcilla et al., 1995a), water + ethanol + acetone + sodium chloride (Olaya et al., 1996), and water + acetone + 1-butanol + sodium chloride (Marcilla et al., 1995b). All these systems contain, at least, the following regions: a one-liquid region; a two-liquid region; a one-liquid−one-solid region; a two-liquid−one-solid region.

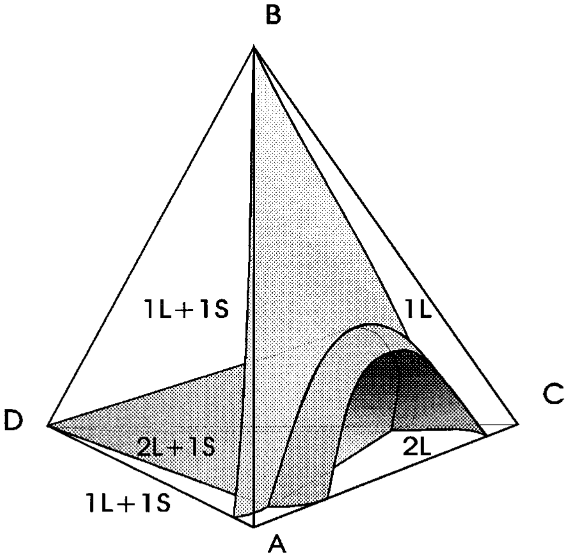

Figure 1. Qualitative phase equilibria of a quaternary liquid−liquid−solid system of the type water (A) + ethanol (B) + 1-butanol (C) + sodium chloride (D).

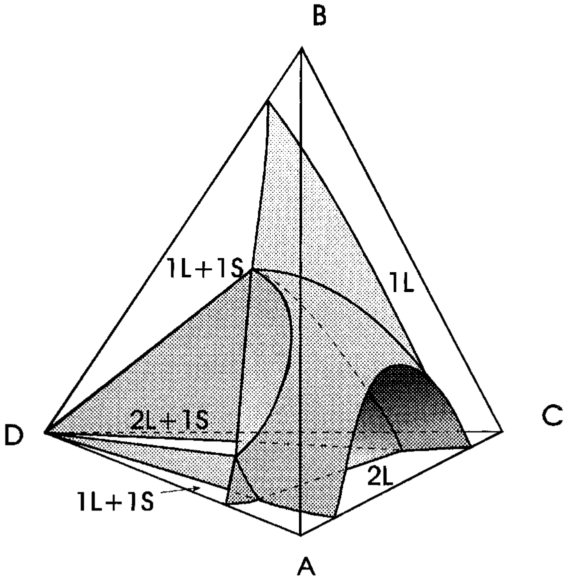

Figure 2. Qualitative phase equilibria of a quaternary liquid−liquid−solid system of the type water (A) + acetone (B) + 1-butanol (C) + sodium chloride (D).

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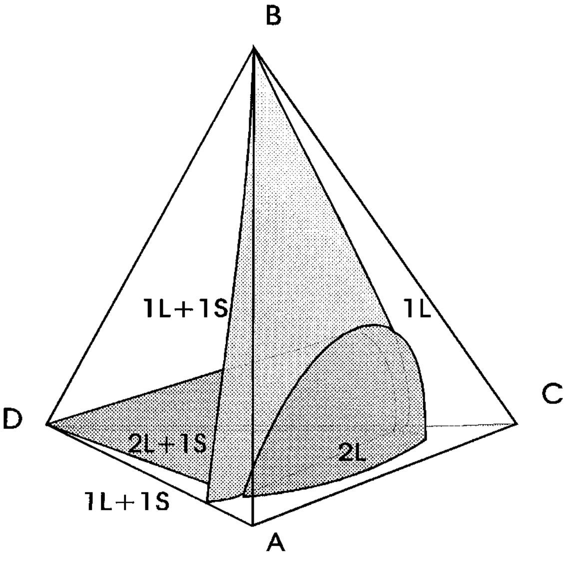

Figure 3. Qualitative phase equilibria of a quaternary liquid−liquid−solid system of the type water (A) + ethanol (B) + acetone (C) + sodium chloride (D).

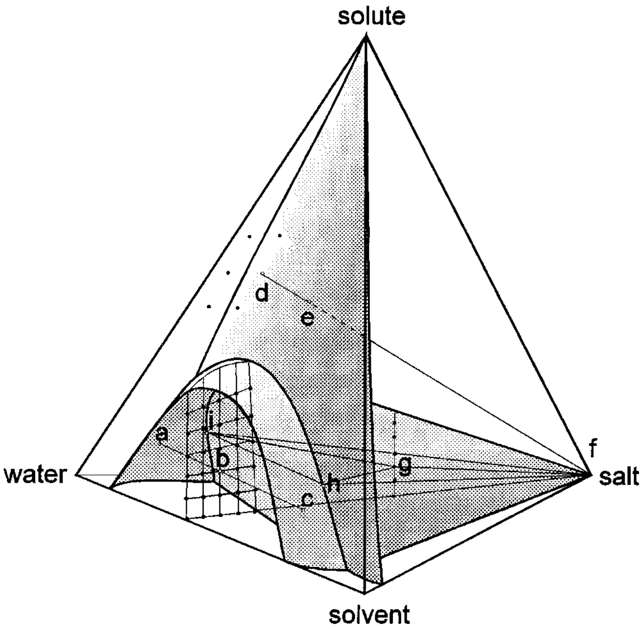

Figure 4. Schematic representation of the methodology to study these types of quaternary systems.

These regions are separated by different solubility surfaces and different tie lines, and tie triangles exist in the different regions, relating the compositions of the phases in equilibrium. To study these equilibria extensively, all surfaces and tie data in the different regions must be determined. In the two-liquid region the behavior is similar to any quaternary liquid−liquid equilibrium, and the methodology that should be used is similar to that suggested by Ruiz and Prats (1983) for liquid−liquid quaternary systems. Figure 4 shows the network to be used to determine the quaternary tie lines. A global mixture represented by a point such as b splits into two phase of compositions given by points a and c. Thus, by determining the compositions of the conjugated phases corresponding to the knots of the network, the two-liquid region can be systematically studied.

The two-liquid−one-solid region is determined by tie triangles connecting the salt vertex to the two-liquid conjugated phases on the limiting solubility curve with the two-liquid region. In order to study this region, it is necessary to determine this limiting curve and the liquid conjugated phases on it. To do this, samples such as g in Figure 4 must be prepared within this region. Such a mixture will split into two liquids (h and i) and one solid (f) phase. Finally, to determine the tie lines in the region of one liquid and one solid phase it is necessary to determine the solubility surface separating the one-liquid and one-liquid−one-solid region, since in this region all the tie lines have the salt vertex as a common end.

There is no reason for any equilibrium region to fulfill any geometric restriction. Nevertheless, we believe that the phase behavior in four-component systems is not always well understood and the triviality of the above comment is not always evident. It is a common practice when studying four-component systems to consider the system as a pseudoternary system (by grouping water + salt as a single component) and to study only the region of two liquids and perhaps the two-liquid−one-solid region, without taking into account that the water and the salt do not distribute in the same proportion between the phases at equilibrium. When carrying out such a study, it is also common to use the titration method to determine the solubility. Only if both the titrating and titrated mixtures are prepared in a quaternary plane will the resulting end equilibrium point be in that quaternary plane. In the work of Sharma et al. (1996) salt crystals were always present in the system. It is evident that they were studying the curve separating the two-liquid and one-solid region. There is no reason for this curve to be on a quaternary plane, and obviously, there is no reason to be on a quaternary plane parallel to the face of the tetrahedron opposite to the salt vertex (i.e. to be on a plane with a constant concentration of salt) such as the authors claim in their Table 2. Moreover, as we stated in another paper, there is no reason for the ends of a tie line prepared on given quaternary plane to lie on such a plane, and consequently, the methodology for determining tie-line data by analyzing the composition of one component and obtaining the others from the solubility curve cannot be applied for quaternaries (when considered as pseudoternaries), since the plane used to determine the solubility curve does not include the ends of the tie lines obtained from the initial mixtures located on that plane. This point is frequently not considered, and the data that are obtained in that way are, consequently, meaningless. Another frequent practice, associated with a misunderstanding of the behavior of the system, is not to provide the concentration of the salt in the conjugated phases (they are wrongly considered to be on a given plane), as well as not to provide the concentration of the initial mixtures in the quaternary region. In Sharma et al. (1996) the tie-line data are supposed to be obtained from the solubility curve in their Table 2 and the composition of one component. That curve is not on a plane. Other mistakes have occurred in other papers (Escudero et al., 1996) such as wrong qualitative trends, contrary to the phase rule, of the equilibrium lines separating the regions of two liquids and two liquids−one solid, which should be straight lines. In summary, to study these type of systems, it is necessary to understand their behavior and spatial geometry and to study qualitatively, quantitatively, and systematically all the equilibrium regions involved and provide consistent equilibrium data.

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Reply to “Letter to Editor” by F. Ruiz and A. Marcilla on *J. Chem. Eng. Data* 1996, *41*, 2−5

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Ruiz and Marcilla explain the objections to considering quaternary systems as pseudoternary systems, in their comment on our work, *J. Chem. Eng. Data* **1996**, *41*, 2−5.

We would like to indicate that we totally agree with their thesis since, in fact, as they state in their letter “there is no reason for the ends of the tie line prepared on a given quaternary plane to lie on such a plane”. However, in the quaternary system, whose three quaternary solubility curves were experimentally determined in our work, the aqueous surface which limits the two phase zone is very narrow and almost coincident with the water−2,3-butanediol tetrahedron edge, as can be easily deduced from the qualitative Figure 6 of our work and by observing that the aqueous phase in the three quaternary solubility curves measured are nearly coincident (Figures 3−5 of our work). This is the reason why all the aqueous phase ends of the tie lines can be considered to be in a line, without significant error, thus permitting us to treat the quaternary system as a pseudoternary one.

In any case, we are now studying the ternary systems resulting from the quaternary system studied in our previous work and a more complete study will soon be published.

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