

THE PHASE BEHAVIOR OF WATER AND HYDROCARBON SYSTEMS

C. L. Young
Department of Physical Chemistry
Parkville, Victoria, 3052
Australia

In order to understand solubility in hydrocarbon + water systems at high pressure it is desirable to be aware of the various types of fluid phase equilibria possible in binary mixtures. Fluid phase equilibria of binary mixtures are conveniently discussed in terms of the classification proposed by Scott and van Konynenburg¹⁻⁴. They proposed that the phase behavior of binary mixtures could be classified into six broad groups. They found that five groups could be predicted using the van der Waals equation of state. The sixth class, which could not be predicted by the van der Waals equation, arises only in aqueous mixtures. The classification is most easily understood in terms of the pressure-temperature projection of the pressure-temperature-composition diagram. The six types of phase behavior are represented schematically in fig. 1. Only the "general" characteristics of the type of phase behavior can be understood from the diagrams given below. In practice solid phases often complicate the diagrams.

Type I. The phase diagram has a simple continuous gas-liquid critical locus with or without azeotropy.

Type II. The phase diagram is as for type I but with the addition of a three phase (liquid-liquid-gas) line ending at an upper critical end point, UCEP, and a (liquid-liquid) critical line starting from the UCEP and rapidly approaching high pressures. This type can occur with or without azeotropy.

Type III. This phase diagram has two distinct critical lines, one starts at the critical point of the pure component with the higher critical temperature but never approaches the critical point of the other component moving rapidly to high pressures. The other critical line starts at the critical point of the component with the lower critical temperature and meets a three phase (liquid-liquid-gas) line in an UCEP. The three phase line may be between the vapor pressure curves of the two components (as shown in fig. 1C) or may be above the vapor pressure curves of both components. There are several subgroups in type III behavior depending on whether there is a heteroazeotrope or not and on the shape of the critical line starting at the critical point with the higher temperature.

Type IV. This phase diagram has three distinct critical loci, one of which (the liquid-liquid critical line) starts at an UCEP on a three phase (liquid-liquid-gas) line and moves rapidly to higher pressures. The second line starts at the critical point of the component with the lower critical temperature and ends at an UCEP on a three phase line. The third line starts at the critical point of the other component and ends in a lower critical end point, LCEP, on the same three phase line as the second critical line.

Type V. This type is the same as type IV but without the liquid-liquid critical line and the three phase line at lower temperatures.

Type VI. This type of phase behavior is characterized by a continuous critical locus between the critical point of the two pure components. However, at lower temperatures there is a three phase line which is bounded above and below by critical end points. A liquid-liquid critical line joins these two critical end points. There are several known configurations of the line joining the ends of the three phase line. In the example illustrated (fig. 1F) the liquid-liquid critical line has two branches with a region of complete liquid miscibility between them.

Most hydrocarbon + water systems studied to date exhibit type III phase behavior. Typical pressure-temperature-composition diagrams for type III behavior are illustrated in fig. 2A and 2B. The most common type of phase behavior found in hydrocarbon water mixtures corresponds to fig. 2A. The behavior shown in fig. 2B has not yet been observed in hydrocarbon + water systems. From fig. 1 and 2 it can be seen that the three phase line on the pressure-temperature projection is derived from three lines on the pressure-temperature-composition diagram representing, the composition of gas, liquid 1 and liquid 2.

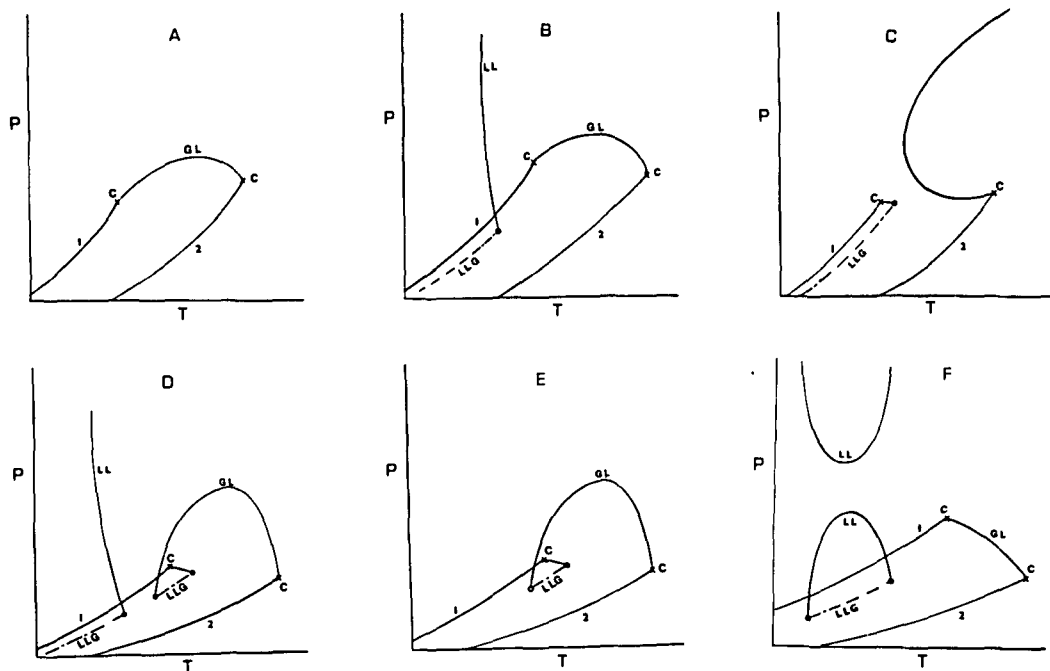


Fig. 1. Pressure-temperature projections for the six types of phase equilibria in binary mixtures. A - Type I; B - Type II; C - Type III; D - Type IV; E - Type V; F - Type VI. Lines labelled 1 and 2 are the vapor pressure of the two components; lines labelled LLG, GL and LL are three phase lines, gas-liquid critical loci and liquid-liquid critical loci respectively; points denoted C are critical points of the pure components.

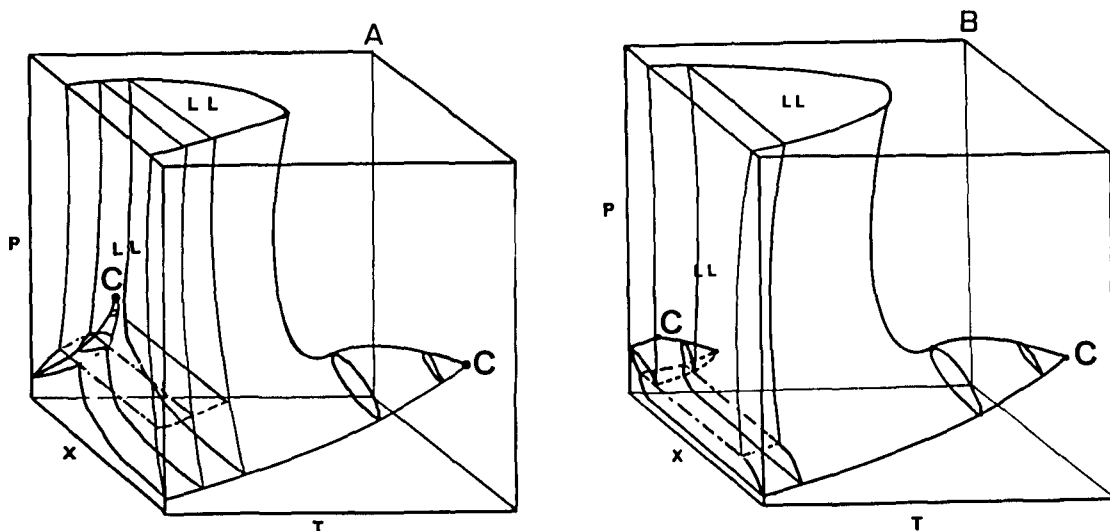


Fig. 2. Pressure-temperature-composition diagrams for two Type III systems. The three phase line is denoted -.-.-. The region in which two liquids coexist is denoted LL.

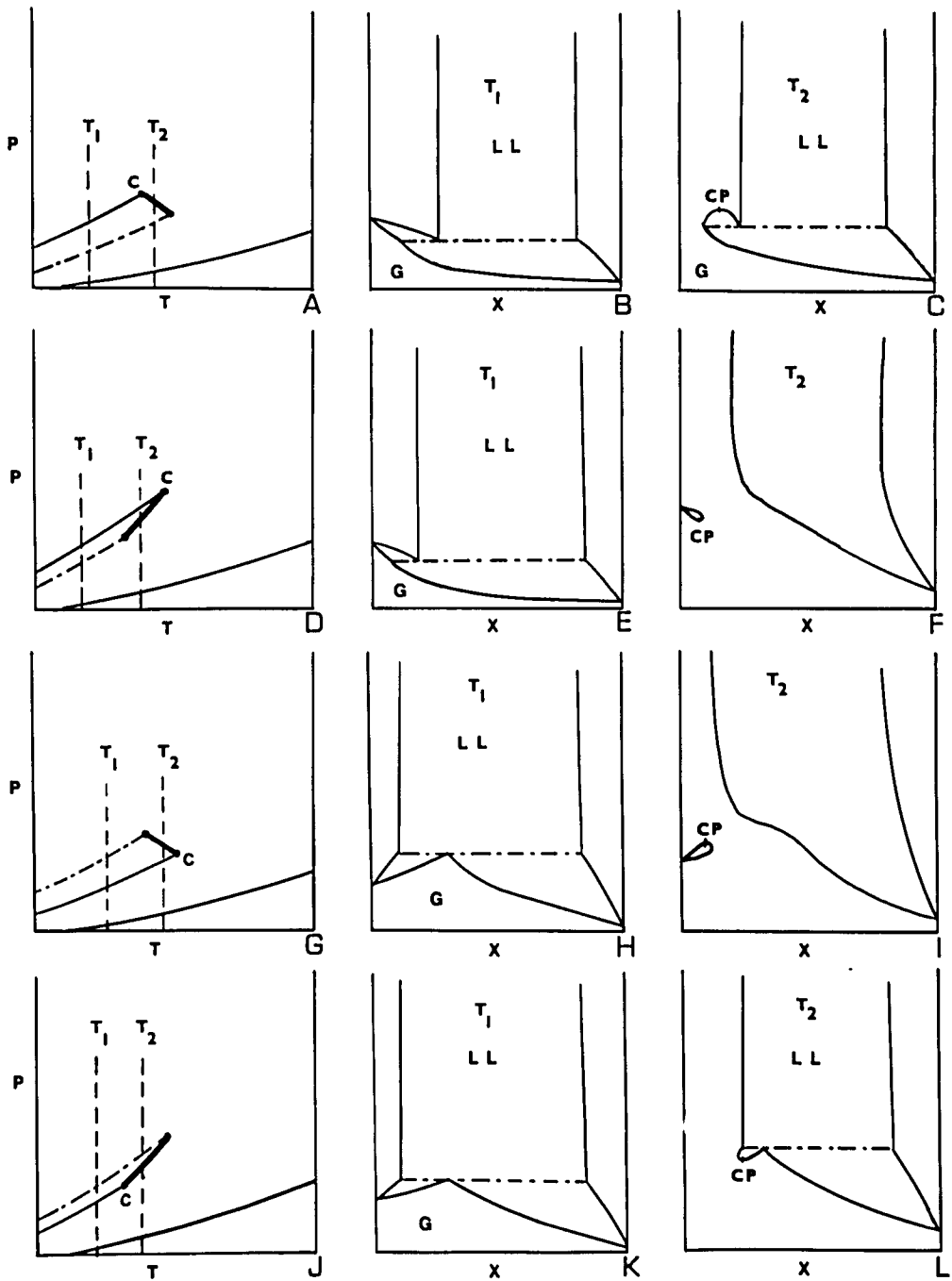


Fig. 3. The four possibilities for the relative position of the three phase line and vapor pressure curves of pure components for type III phase behavior. Figures A, D, G and J are pressure-temperature projections of the four classes. Figures B, E, H and K are the constant temperature, T_1 , sections of the p, T, X diagrams; fig. C, F, I and L are analogous sections at temperature T_2 . Most hydrocarbon systems have behavior illustrated in fig. 3G, 3H and 3I.

There are many sub-types of type III behavior. Consider the portion of the phase diagram in the region of the upper critical end point and the critical point of the pure component with the lower critical temperature. There are four possibilities. The three phase line could be at higher or lower pressures than the vapor pressure curve of the pure component. Each of these two cases could have the upper critical end point at a higher (or lower) temperature than the critical point. These four possibilities are illustrated in fig. 3. The position of the vapor pressure of the second component can be above or below that of the first component. In the case of hydrocarbon + water systems the two pure component vapor pressure curves sometimes cross on the pressure-temperature projection (e.g. benzene + water). Most hydrocarbons + water systems exhibit the behavior illustrated in fig. 3G. Consider fig. 3G, the three phase line is at higher pressures than the vapor pressure of the pure component (1). At a temperature, T_1 , the pressure-composition diagram is shown in fig. 3H. It can be seen that depending on the pressure and overall composition it is possible to have one, two, or three phases present. At high pressures we have a fluid-fluid equilibrium which if T_1 is sufficiently low, it is reasonable to refer to as a liquid-liquid equilibrium. Although a line parallel to the composition axis at pressures between the three phase line and the vapor-pressure of component (1) cuts the boundary lines in four places, only two phases can be in equilibrium. The two phases in equilibrium will depend on the overall composition. At temperature T_2 a different situation exists in that at pressures above the critical line it is possible to have two phases present (fig. 3I). At pressures below the critical point it is possible to have two phases coexisting out of a possible four phases. Which are the two coexisting phases depends on the overall composition. At some compositions only one phase will be present.

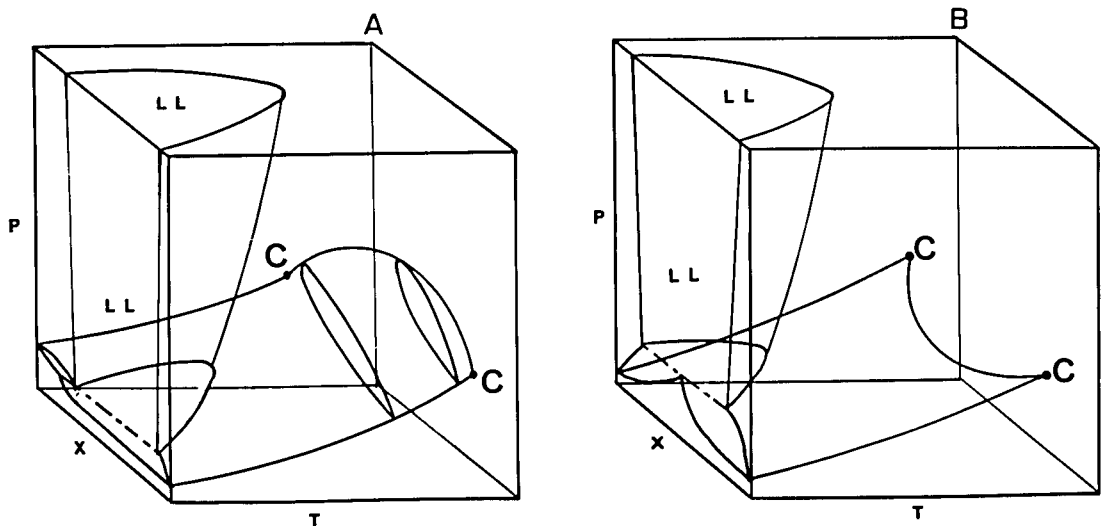


Fig. 4. Pressure, temperature, composition diagrams for two Type II systems. The three phase line is denoted -.-.-. The region in which two liquids coexist is denoted LL.

Although most hydrocarbon + water systems studied to date exhibit type III phase behavior it is known that some hydrocarbons of greater molecular weight, such as biphenyl exhibit type II phase behavior⁶. Figures 4A and 4B illustrate the pressure-temperature-composition diagram for two type II systems. It appears that most, if not all, hydrocarbon + water systems which exhibit type II behavior have a minimum in temperature for the gas-liquid critical curve which corresponds to the behavior illustrated in fig. 4B.

Some hydrocarbon + water systems have been observed to exhibit the phenomenon referred to as gas-gas immiscibility^{6,7}. This phenomenon^{5,8} occurs in type III phase behavior when the critical locus starting at the component with the highest critical temperature initially or eventually moves to high pressure at temperatures above the critical point of either component. If the critical locus always has a positive slope on the pressure-temperature projection the phenomenon is referred to as gas-gas immiscibility of the first kind (fig. 5A) whereas if the locus initially moves to lower temperatures, goes through a minimum and eventually moves to temperatures greater than the critical temperature of either component the mixture is said to exhibit gas-gas immiscibility of the second kind (fig. 5B). Gas-gas immiscibility of the second kind is exhibited by some hydrocarbon + water systems.

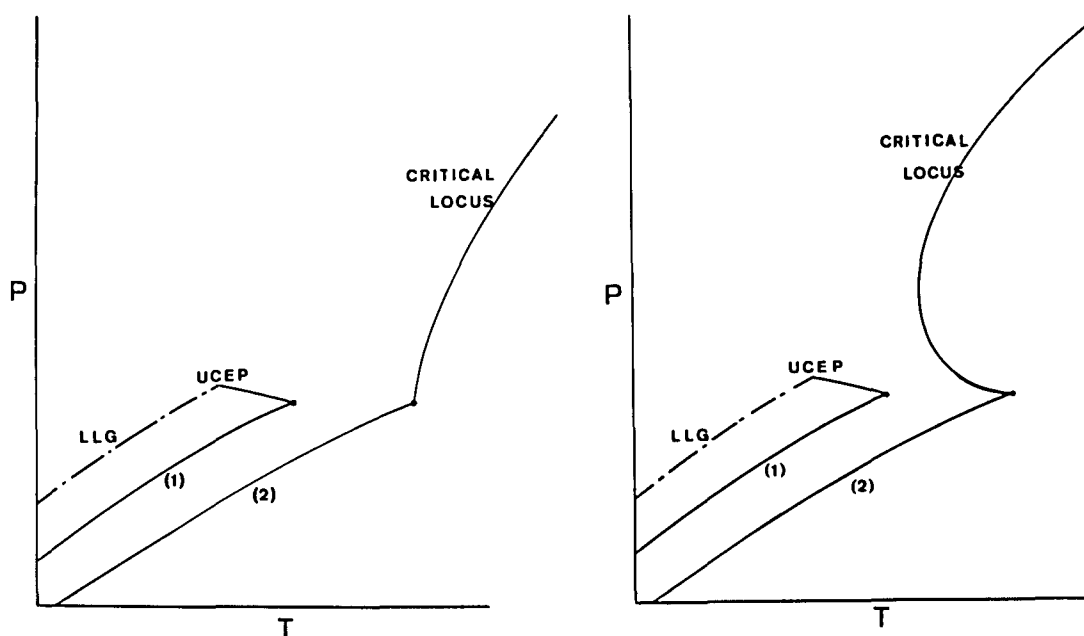


Fig. 5. Pressure, temperature projections for systems exhibiting gas-gas immiscibility. Figure 5A - immiscibility of the first kind. Figure 5B - immiscibility of the second kind.

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