

# Experiment 8

## Ternary Phase Equilibrium : All Liquid Diagram

### Purpose :

In many cases, the addition of a third component to a pair of almost immiscible liquids does not appreciably increase their solubility in each other. However, the addition of a third liquid intermediate in polarity may have a large effect, and such a case is illustrated in this experiment.

### Principle :

According to the phase rule of **Gibbs**, the variance  $f$  (number of degrees of freedom) of a system at equilibrium is equal to the number of components  $c$  minus the number of phases  $p$  plus 2, provided that the equilibrium is influenced only by temperature, pressure, and concentration.

$$f = c - p + 2 \quad (1)$$

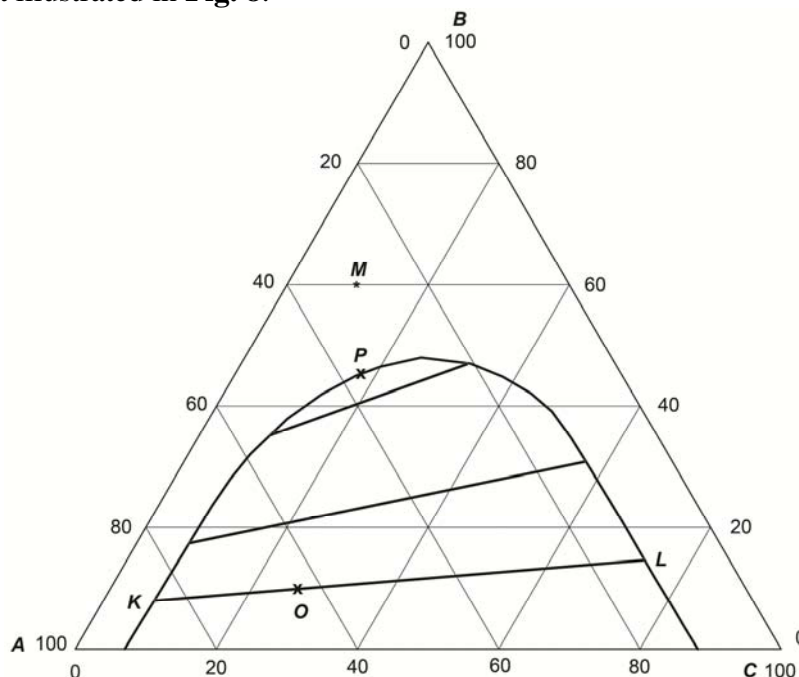
The variance  $f$  is the smallest number of independent variables required to completely describe the state of the system.

This experiment is carried out at constant temperature and pressure so that these are not variables. Thus Eq. (1) becomes

$$f = c - p \quad (2)$$

so that for a three-component system  $f = 3 - p$ . Thus the variance is 2 if a single phase is present and 1 if two phases are present.

It is convenient to represent a three-component system on a triangular diagram such as that illustrated in **Fig. 8**.



**Fig. 8 Phase Diagram for a Three-Component System**

In an equilateral triangle, the sum of the perpendiculars from a given point to the three sides is a constant. The perpendicular distance from each apex, representing a pure compound, to the opposite side is divided into 100 equal parts, corresponding to per cent, and labeled along the side at the right of the perpendicular. A point situated on one of the sides of the triangle indicates that there are two components with the percentage composition indicated. The composition corresponding to any point within the triangle is obtained by measuring on these coordinates the distance toward apex *A*, the distance toward *B*, and the distance toward *C*. These three distances representing percentages always add up to 100. For example, Point *M* represents the composition 30 per cent *A*, 60 per cent *B*, and 10 per cent *C*.

Several different types of ternary systems are possible, depending upon whether one, two, or three pairs of the liquids are partially miscible in each other. In the system illustrated in Fig. 8, *A* and *C* are partially miscible while pair *A* and *B* and pair *B* and *C* are completely miscible. Mixtures having compositions lying below the curve will separate into two phases, while all other mixtures form homogeneous solutions. For example, mixture *O* will separate into two phases *K* and *L*, and the line connecting these conjugate ternary solutions in equilibrium with each other is called a tie line. It is an important characteristic of a ternary diagram that the relative amounts of phases *K* and *L* are proportional to the lengths *OL* and *OK*, respectively. These tie lines slope upward to the right, indicating that component *B* is relatively more soluble in the phase rich in *C* than it is in the phase rich in *A*.

As the amount of component *B* is increased, the compositions of the conjugate solutions approach each other. At point *P* the two conjugate solutions have the same composition, so that the two layers have become one: this is called the plait point.

### ***Apparatus and Chemicals :***

Eighteen 125-ml Erlenmeyer flasks; three 25-ml pipettes; one 10-ml pipettes; two 5-ml pipettes; one 2-ml pipette; one 1-ml pipette; four separating funnels; two safety bulbs; two funnels; two 50-ml burettes.

Toluene; glacial acetic acid; 1*N* NaOH; KHP; phenolphthalein.

### ***Procedures :***

#### **Part A : Determine the solubility curve of the phase diagram.**

(1) Pipette toluene and water into twelve 125-ml Erlenmeyer flasks. The appropriate amounts of toluene and water are given in the table below.

Solutions	Initial volume of solvents, mL											
	1	2	3	4	5	6	7	8	9	10	11	12
Toluene	15	15	10	10	5	5	3	3	1	1	1	1
Water	1	2	2	3	2	3	3	6	5	10	17	25

- (2) Titrate carefully and slowly with glacial acetic acid. During the titration, the flask is shaken vigorously and the end point is taken until a clear solution is obtained.

**Part B : Determine the tie lines.**

- (1) Mix toluene, glacial acetic acid, and water in four separating funnels with the total volume 40 ml and shake vigorously. The percentages by volume of each component are as follows: (toluene, glacial acetic acid, water); (40, 20, 40); (40, 30, 30); (40, 40, 20); (40, 50, 10).
- (2) After the solution separate into two layers, remove about 5 ml sample of the lower layer into an Erlenmeyer flask and weigh the sample.
- (3) Titrate the samples obtained from **step (2)** with 1N NaOH, using phenolphthalein as indicator.
- (4) Repeat **step (3)** by titrating each upper layers if time is enough.
- (5) Standardize 1N NaOH solution: Add accurately 2g KHP into distilled water and titrate with NaOH, using phenolphthalein as and indicator.

**Calculations :**

- (1) The percentages by weight of toluene, glacial acetic acid, and water for each of the mixtures that showed the first indication of clarity are calculated and plotted on triangular graph paper. The densities of each liquids are  $d_{\text{Toluene}} = 0.867$ ,  $d_{\text{HOAc}} = 1.049$ , and  $d_{\text{H}_2\text{O}} = 0.996$  g/ml.
- (2) The tie lines should pass through each three points which are calculated from the **steps B-(3), B-(4)**, and the original composition given by **step B-(1)**.
- (3) Determine the plait point (critical point) on the curve.

**References :**

- (1) **I. N. Levine**, "*Physical Chemistry*," 6th ed., pp. 385-387, McGraw-Hill, U.S.A. (2009).
- (2) **A. W. Davison** and others, "*Laboratory Manual of Physical Chemistry*," 4th ed., pp. 106-109, John Wiley & Sons, Inc., U.S.A. (1956).
- (3) **F. Daniels** and others, "*Experimental Physical Chemistry*," 6th ed., pp. 121-124, Europe-Asia book company, Taiwan (1956).
- (4) **O. F. Steinbach** and **C. V. King**, "*Experiments in Physical Chemistry*," pp. 124-129, American book company, U.S.A. (1950).

