

Experiment

Phase diagram for a three-component system



Prepared By:

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Date:

Room Temperature: 30 °C

Objective: To construct the phase diagram for a three-component liquid system, consisting of Chloroform, Acetic acid, and Water.

Requirements:

(a) Apparatus and Glassware: Ten glass-stoppered bottles, Three burettes, Separating funnel, Conical flask, Pipette, Thermostat bath (room temperature), Beaker.

(b) Chemicals:

- Chloroform (CHCl₃) (molecular weight = 119.38 g mol⁻¹)
- Acetic Acid (CH₃COOH) (molecular weight 60.05 g mol⁻¹)
- Distilled water (H₂O) (molecular weight = 18.016 g mol⁻¹)
- 1.0 N NaOH and 1.0 N Oxalic acid (H₂C₂O₄.2H₂O)

1. Principle**1.1 Phase Rule:**

Information regarding phase equilibria can be predicted by following phase rule of Gibbs:

$$F = C - P + 2 \quad (1)$$

where C is the number of components and P is the number of phases present in the system. The degrees of freedom F , or variance, gives the number of variables (*e.g.*, pressure, temperature, composition, *etc.*) that must be given to completely describe the system, or to locate the state of the system on the phase diagram.

For ternary systems (*i.e.*, consisting of three components), we have $C = 3$ and $F = 5 - P$. If the system consists of only one phase, $F = 4$. The required four variables for describing such system are: two for describing the relative composition (mass fractions) and one of the pairs (*pressure, volume*), (*pressure, temperature*), or (*temperature, volume*). Therefore, graphical representation of ternary system requires four-dimensional diagram and that is very difficult to draw in simple paper-pencil.

Generally, the three-component system experiment is conducted at constant pressure (open atmosphere, *i.e.*, 1 atm) and constant temperature so that these are not variable. Thus, Eq. (1) becomes

$$F = C - P + 2 - 2 \quad (2)$$

$$F = C - P \quad (3)$$

and for a three component system $F = 3 - P$. Thus in a three-component system, if only one liquid phase is present, $F = 2$ and the concentration of two of the chemical substances must be specified in order to describe the system completely. If two immiscible liquid phases are present in equilibrium, $F = 1$ and the concentration of the only one component need to be specified – the concentration of the others may be ascertained by reference to the phase diagram.

1.2. Method of graphical representation of three-component system

The behavior of a three-component system at constant temperature and pressure can be represented in a planar triangular diagram with three co-ordinates as illustrated in **Fig. 1**. This graph accounts for the fact that only two variables are required. And along the phase boundary only one variable is required.

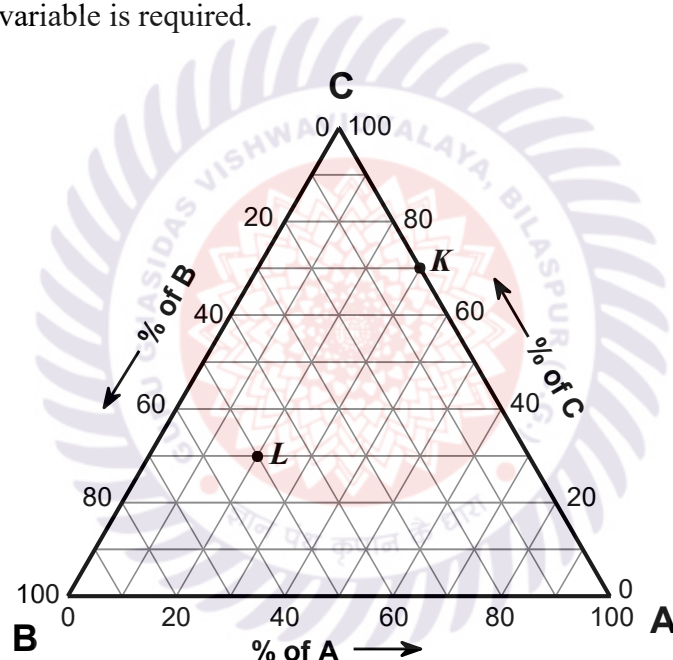


Fig. 1. Representation of a three-component system in a triangular phase-diagram.
(Pressure and temperature are assumed to be fixed)

In the diagram above, the three apexes (corners) of the triangle represent a pure component each, i.e. 100 % by weight of one component (A , B , or C). The three lines joining the corner points represent two-component mixture of the three possible combinations of A , B , and C . The perpendicular distance from each apex to the opposite side is divided into 100 equal parts, corresponding to percent, and labeled along the side at the right of the perpendicular. The area within the triangle represents all the possible combinations of A , B , and C to give three-component system.

In an equilibrium stage of triangle, the sum of the perpendiculars from a given point to the three sides is a constant. A point situated on one of the sides of the triangle indicates that there are two components with percentage composition. The composition corresponding to any point within the triangle is obtained by measuring on these coordinates the distance toward apex *A*, the distance toward apex *B*, and the distance toward apex *C*. For examples, point *K* indicates 70 % *C*, 30 % *A*, and 0 % *B*; point *L* represents the composition 20 % *A*, 50 % *B*, and 30 % *C*.

2. Solution Preparation

2.1. 1.0 N NaOH in 250 mL

$$w = \frac{\text{Normality} \times \text{Equiv. Wt.} \times \text{Volume}}{1000}$$

$$w = \frac{1.0 \times 40 \times 250}{1000} = 10 \text{ g}$$

Dissolve approximately 10 g of NaOH in 250 mL volumetric flask with distilled water and make up to the mark with distilled water. (Standardization is required).

2.2. 1.0 N H₂C₂O₄·2H₂O (oxalic acid) in 50 mL

$$w = \frac{1.0 \times 63 \times 50}{1000} = 3.15 \text{ g}$$

Dissolve 3.150 g of oxalic acid in 50 mL volumetric flask with distilled water and make up to the mark with distilled water.

3. Experimental Procedure

3.1. Preparation of phase diagram:

- (i) Set up burettes containing CHCl₃, CH₃COOH, & H₂O.
(CAUTION: Glacial acetic acid is corrosive).
- (ii) Make up accurately in the clean and dry stoppered glass bottles, mixtures of CHCl₃ and CH₃COOH containing 1.5, 2.0, 2.5, 3.5, 6.5, 9.5, 13.0, and 16.0 mL of CHCl₃, the total volume of each mixture being 20 mL. Kept these bottles to in thermostat to allow equilibrating at room temperature.

- (iii) After attaining to room temperature, titrate each mixtures with H₂O (shaking well after each addition) until the homogenous solution becomes permanently turbid. Note the volumes of water added. Note the room temperature.

(The turbidity results from scattering of light by the large number of very small "oily" droplets of the second phase that are produced when the system is stirred. Sometimes it is easier to see this when stopping the stirring briefly.)

- (iv) From the volumes and densities of CHCl₃, CH₃COOH, & H₂O, calculate the weight percent of compositions of the ternary mixtures, and plot them on triangular graph paper. Draw the complete Isotherm. Given that at room temperature a saturated solution of chloroform in water contains 0.809 g CHCl₃ in 100 mL H₂O (20 °C), and a saturated solution of water in chloroform contain 1.0 g H₂O in 100 mL CHCl₃.

3.2 Determination of tie-lines:

- (i) Using the burette as before, make up accurately in clean and dry two bottles having the mixtures of the compositions (X) and (Y) as following:

Bottle	Compositions	CHCl ₃	CH ₃ COOH	H ₂ O
		mL	mL	mL
1	X	6.5	3.5	10.0
2	Y	5.5	7.5	7.0

Then shake each bottle for 30 minutes and let the solution settle for two separate layers.

- (ii) Mean while, prepare 250 mL of approximately 1.0 N Sodium hydroxide solution and standardize with 1.0 N oxalic acid, using phenolphthalein as indicator.
- (iii) Separate layers of the above X and Y composition by a separatory funnel (which should be clean and dry in each time).
- (iv) Then weigh accurately four clean and dry conical flasks and their corks. Run exact 5.0 mL of each layers of compositions in a conical flask and reweigh. (**Table: 2**)
- (v) After weighing conical flasks, titrate the acid in each conical flask with the standardized NaOH solution, using phenolphthalein as indicator. (**Table: 3**)
- (vi) From the titers, calculate the weight percent of acetic acid in each layer. This fixes the positions on the isotherm of the ends of the tie-lines, since it is known which layers are H₂O-rich and CHCl₃-rich, indicate the ends (P and Q for composition X) and (R and S for composition Y) and join them by straight lines.

4. Calculation and Observation Table

4.1 Drawing of phase-diagram

Mass fractions for CHCl_3 , CH_3COOH , and H_2O in different mixture are summarized in **Table 1**. Mass fractions (in %) for each component in every solution can be calculated using the following equation:

$$\text{Mass Fraction (in \%)} = \frac{V_i \rho_i}{\sum_{i=1}^3 V_i \rho_i} \times 100$$

where V_i is the volume and ρ_i the density of the component i (CHCl_3 , CH_3COOH , & H_2O). The densities of CHCl_3 , CH_3COOH , & H_2O are 1.4892, 1.1491, 0.9947 g/mL, respectively.

From the obtained mass fraction (in %) of CHCl_3 , CH_3COOH , & H_2O draw a triangular graph. **Fig. 2** shows a triangular phase-diagram of experimental CHCl_3 - CH_3COOH - H_2O ternary system.

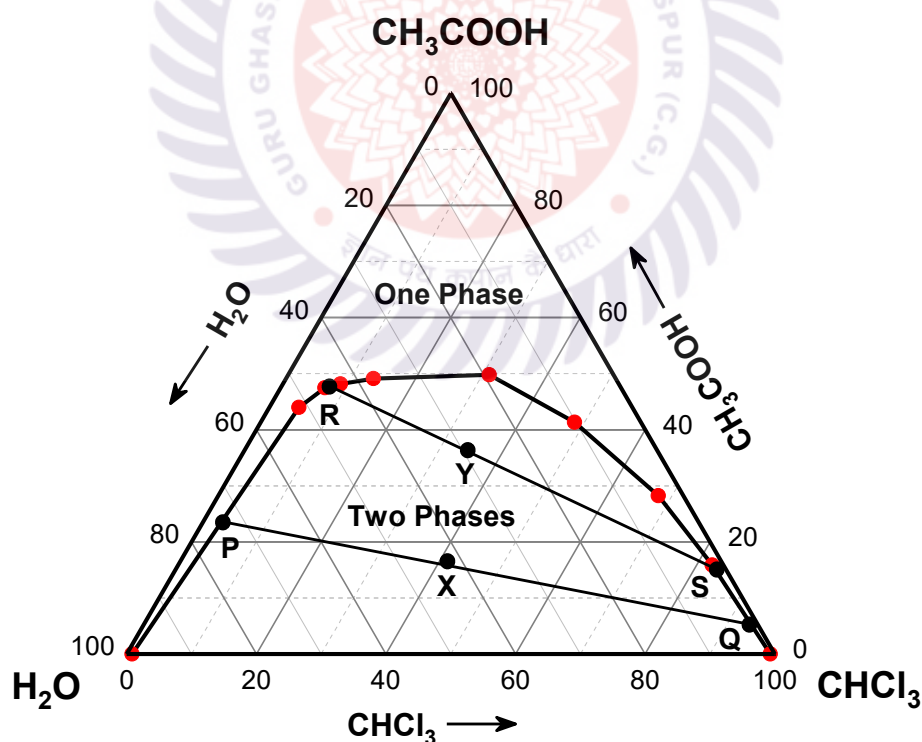


Fig. 2. A triangular phase diagram for CHCl_3 , CH_3COOH , & H_2O ternary system. Lines PQ and RS are representing tie-lines for compositions X and Y, respectively.

Table 1: Calculation of mass fractionDensity of Water ρ_1 0.9947 g/mL, 30 °CDensity of Acetic Acid ρ_2 1.1491 g/mL, 30 °CDensity of Chloroform ρ_3 1.4892 g/mL, 30 °C

Bottle No.	Composition	Volume	Mass	Total Mass	Mass Fraction
		V_i	$V_i\rho_i$	$\sum_{i=1}^3 V_i\rho_i$	$\frac{V_i\rho_i}{\sum_{i=1}^3 V_i\rho_i} \times 100$
		mL	g	g	%
Saturated Solution of CHCl_3 in H_2O	CHCl_3	0.54	0.804	99.737	0.806
	CH_3COOH	0.00	0.000		0.000
	H_2O	99.46	98.933		99.194
1	CHCl_3	1.50	2.234	48.360	4.619
	CH_3COOH	18.50	21.258		43.959
	H_2O	25.00	24.868		51.422
2	CHCl_3	2.00	2.978	43.556	6.838
	CH_3COOH	18.00	20.684		47.488
	H_2O	20.00	19.894		45.674
3	CHCl_3	2.50	3.723	41.737	8.920
	CH_3COOH	17.50	20.109		48.181
	H_2O	18.00	17.905		42.899
4	CHCl_3	3.50	5.212	38.596	13.505
	CH_3COOH	16.50	18.960		49.125
	H_2O	14.50	14.423		37.370
5	CHCl_3	6.50	9.680	31.161	31.064
	CH_3COOH	13.50	15.513		49.783
	H_2O	6.00	5.968		19.153
6	CHCl_3	9.50	14.147	29.197	48.455
	CH_3COOH	10.50	12.066		41.325
	H_2O	3.00	2.984		10.221
7	CHCl_3	13.00	19.360	28.497	67.934
	CH_3COOH	7.00	8.044		28.226
	H_2O	1.10	1.094		3.840
8	CHCl_3	16.00	23.827	28.921	82.387
	CH_3COOH	4.00	4.596		15.893
	H_2O	0.50	0.497		1.720
Saturated Solution of H_2O in CHCl_3	CHCl_3	98.99	147.416	148.421	99.323
	CH_3COOH	0.00	0.000		0.000
	H_2O	1.01	1.005		0.677

4.2. Preparation of tie-lines

Standardization of NaOH

Standardization is the process of determining the exact concentration (normality/molarity) of a secondary standard solution. In our experiment, exact normality of the NaOH is obtained by the acid-based titration as given below. The exact normality of prepared NaOH is obtained 0.9.

Titration of oxalic acid *versus* NaOH

Indicator: Phenolphthalein

S. No.	Volume of 1.0 N oxalic acid (V ₁)	Burette Reading		Used volume of NaOH (V ₂)
		Initial	Final	
	mL	mL	mL	mL
1	10	0	11.3	11.3
2	10	0	11.0	11.1
3	10	0	11.0	11.1

$$N_1V_1 (\text{Oxalic acid}) = N_2V_2 (\text{NaOH})$$

$$1.0 \times 10 = N_2 \times 11.1$$

$$N_2 = 0.9 \text{ N}$$

Thus, mass fraction of acetic acid present in the CHCl₃-rich and H₂O-rich layers in the composition X and Y can be obtained by simple $N_1V_1 = N_2V_2$ relation and the results are summarized given in **Table 2** and **Table 3**. The tie-lines PQ and RS for the compositions X and Y, respectively are plotted and shown in the Fig 1.

Table 2: Weight of upper and lower layers of compositions X and Y

S. No	Composition Layer	Rich Layers	Weight of empty conical flask	Weight of conical flask with 5 mL composition	Absolute weight of 5 mL composition
		g	g	g	g
1	X-Upper	H ₂ O-rich	125.239	130.117	4.878
2	X-Lower*	CHCl ₃ -rich	123.984	130.649	6.665
3	Y-Upper	H ₂ O-rich	122.875	127.853	4.978
4	Y-Lower	CHCl ₃ -rich	129.415	135.652	6.237

* Denser liquid is reside in the lower part

Table 3: CH₃COOH present in each layer of composition X and Y

Aliquot 5 mL composition

Point	Layer	Absolute weight of 5 mL composition	Titer value of NaOH	Concentration of Acid	Weight of acid present in 5 mL aliquot	Mass fraction of acid
		g	mL	N	g/5 mL	%
P	X-Upper	4.878	22.3	4.014	1.204	24.686
Q	X-Lower	6.665	6.4	1.152	0.346	5.185
R	Y-Upper	4.978	43.3	7.794	2.338	46.971
S	Y-Lower	6.237	19.3	3.474	1.042	16.710

5. Result and Discussion

Fig. 2 shows the phase-diagram and tie lines for the experimental CHCl₃, CH₃COOH, & H₂O ternary system. This is an example of ternary liquid system, where one pair of liquids is partially miscible to each other. In this system, pair H₂O-CH₃COOH and pair CHCl₃-CH₃COOH are completely miscible at all concentrations, while pair H₂O-CHCl₃ is partially miscible and form two liquid phases which do not mix with each other. All mixtures of these three liquids having composition lying below the curve shown in Fig. 1 will separate in two separate liquid phases, while all mixtures having compositions lying above the curve will give one homogeneous liquid phase. The one- and two- phase regions have been separated by a black line in the Fig. 2.

For example, mixture X will separate into two liquid phases, one having the composition P (H₂O-rich) and the other the composition Q (CHCl₃-rich) and line connecting these two immiscible ternary solutions in equilibrium with each other is called a **tie-line**. The tie-line PQ also passes through the gross composition of mixture X which is indicated in triangular graph and this is accordance with the phase rule. The relative amount of phase P is given by the ratio XQ/PQ, and relative amount of phase Q by the ratio XP/PQ. The negative slope of tie-lines i.e. downward to right, indicating that CH₃COOH is more soluble in H₂O-rich phase than CHCl₃-rich phase.

As the amount of CH₃COOH is increased (mixture Y), the length of tie-line is reduced, thus compositions of H₂O-rich and CHCl₃-rich phases approach each other. Finally, a particular composition of CH₃COOH the two conjugate solutions have the same

composition. Therefore, the two layers have become one and this point is called the **plait point**.

Practical Application: The increase in mutual solubility of two liquids due to the addition of a third is of practical as well as theoretical importance. Calculation in two-phase extraction processes may be carried out, using triangular diagrams.

6. Precautions

- The percentage by weight of CHCl_3 , CH_3COOH , & H_2O for each of the mixtures that showed the first indication of turbidity is plotted on the triangular graph paper.

7. Further Reading

- (i) Read up details of the Gibbs phase rule.
- (ii) *Physical Chemistry*, P. W. Atkins and J. D. Paula, Eds: 7th, Oxford University Press.
- (iii) *Principle of Physical Chemistry*, B. R. Puri, L. R. Sharma, and Pathania, Vishal Publishing Co. Jalandhar.
- (iv) *Experimental Physical Chemistry*, F Daniels, R. Alberty, J. W. Williams, C. D. Cornwell, P. Bender, and J. E. Harriman, McGraw-Hill, 1970.
- (v) J. R. Clarke, *J. Chem. Ed.* 51, 255 (1974).