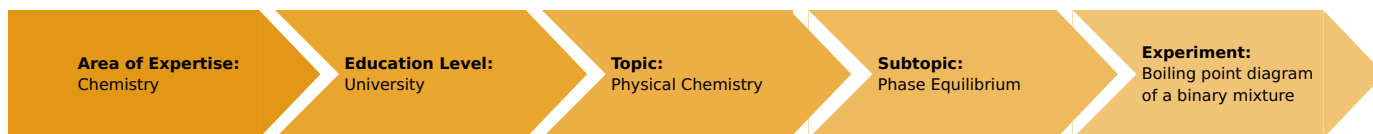


Boiling point diagram of a binary mixture (Item No.: P3030401)

Curricular Relevance



Difficulty



Intermediate

Preparation Time



1 Hour

Execution Time



1 Hour

Recommended Group Size



2 Students

Additional Requirements:

Experiment Variations:

Keywords:

Fundamentals of distillation, Equilibrium diagram, Chemical potential, Activity coefficient, Raoult's law

Task and equipment

Introduction

Principle:

A boiling point diagram shows the boiling points of a binary mixture as a function of the vapour / liquid equilibrium of the mixture at constant pressure. The boiling points of various mixtures of methanol and chloroform are measured and the composition of the liquid phases determined using refractometry and a calibration curve.



Safety instructions



Methanol

H225: Highly flammable liquid and vapour.

H301: Toxic if swallowed.

H311: Toxic in contact with skin.

H331: Toxic if inhaled.

H370: Causes damage to organs.

P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.

P233: Keep container tightly closed.

P240: Ground/bond container and receiving equipment.

P241: Use explosion-proof electrical/ventilating/light/.../equipment.

P242: Use only non-sparking tools.

P243: Take precautionary measures against static discharge.

P260: Do not breathe dust/fumes/gas/mist/vapours/spray.

P264: Wash ... thoroughly after handling.

P270: Do not eat, drink or smoke when using this product.

P280: Wear protective gloves/protective clothing/eye protection/face protection.

P330: Rinse mouth.

P301+310: IF SWALLOWED: Immediately call a POISON CENTER/doctor/...

P302+352: IF ON SKIN: Wash with plenty of water/...

P303+361+353: IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water/ shower.

P304+340: IF INHALED: Remove person to fresh air and keep comfortable for breathing.

P403+235: Store in a well ventilated place. Keep cool.

Chloroform

H302: Harmful if swallowed.

H315: Causes skin irritation.

H319: Causes serious eye irritation.

H331: Toxic if inhaled.

H332: Harmful if inhaled.

H336: May cause drowsiness or dizziness.

H351: Suspected of causing cancer.

H361: Suspected of damaging fertility or the unborn child.

H361d: Suspected of damaging the unborn child.

H372: Causes damage to organs through prolonged or repeated exposure.

H373: May cause damage to organs through prolonged or repeated exposure.

P261: Avoid breathing dust/fumes/gas/mist/vapours/spray.

P311: Call a POISON CENTER/ doctor/...

P305+351+338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do - continue rinsing.

Equipment

Position No.	Material	Order No.	Quantity
1	Abbe refractometer	35912-00	1
2	Temperature meter, digital, 4-2	13617-93	1
3	Temperature probe, Pt100	11759-01	1
4	Protective sleeve for immersion probe	11762-05	1
5	Heating hood, 100 ml	47549-93	1
6	Clamp for heating hood	47557-01	1
7	Power regulator	32247-93	1
8	Immersion thermostat, 100°C	08492-93	1
9	Accessory set for immersion thermostat	08492-01	1
10	Bath for thermostat, 6 l, Makrolon	08487-02	1
11	Retort stand, h = 750 mm	37694-00	2
12	Right angle clamp	37697-00	2
13	Universal clamp	37715-00	2
14	Burette clamp, roller mounting	37720-00	1
15	Round bottom flask, 100 ml, 2-neck, IGJ 19/26	35842-05	2
16	Dimroth cooler, IGJ 19/26	35816-05	1
17	Column head, IGJ 19	35919-01	1
18	Stopper, IGJ 19/26, glass, clear	41252-10	1
19	Clamp for ground joint, plastic, IGJ 19	43614-00	3
20	Teflon collar, IGJ 19	43616-00	1
21	Rubber tubing, d(i) = 6 mm	39282-00	5
22	Hose clip, d = 8...12 mm	40996-01	10
23	Burette, 50 ml, lateral stopcock, Schellbach lines	36513-01	2
24	Erlenmeyer flask, 100 ml, narrow neck	36118-00	11
25	Rubber stopper, 24/30 mm	39256-00	11
26	Glass beaker, 100 ml, tall	36002-00	2
27	Pasteur pipettes	36590-00	1
28	Rubber bulbs	39275-03	1
29	Funnel, glass, d(o) = 55 mm	34457-00	1
30	Beads, 200 g	36937-20	1
31	Water jet pump	02728-00	1
32	Laboratory pencil, waterproof	38711-00	1
33	Methanol, 500 ml	30142-50	1
34	Chloroform, pure, 250 ml	48045-25	1
35	Glycerin, 250 ml	30084-25	1

Task

1. Determine the refractive indices of the pure components and about 10 different mixtures of known composition.
2. Plot the boiling point diagram of the binary mixtures of methanol and chloroform.



Set-up and procedure

Set-up



Set up the experiment as shown in Fig. 1.



Prepare eleven different mixtures of chloroform and methanol. To do this, use two burettes to deliver the quantities of methanol and chloroform listed in Table 1 into Erlenmeyer flasks and seal each with a stopper.

Mixture	Methanol / ml	Chloroform / ml
1	2.5	47.5
2	5	45
3	10	40
4	15	35
5	20	30
6	25	25
7	30	20
8	35	15
9	40	10
10	45	5
11	47.5	2.5

Procedure

Temperature equilibrate the refractometer to 20 °C using a temperature controlled bath.

Determine the refractive indices of pure methanol, pure chloroform and the various mixtures by dropping the liquids onto the prism surface with a clean Pasteur pipette and reading off the measured value after optical adjustment (see the instruction manual of the refractometer). Clean the refractometer thoroughly before each new measurement.

Before pouring a mixture into the boiling point apparatus, drop a few drops of glycerin into the protective sleeve for the temperature probe to improve heat conductivity. Pour the first mixture into the 2-neck flask, add a few boiling beads and switch on the heating hood.

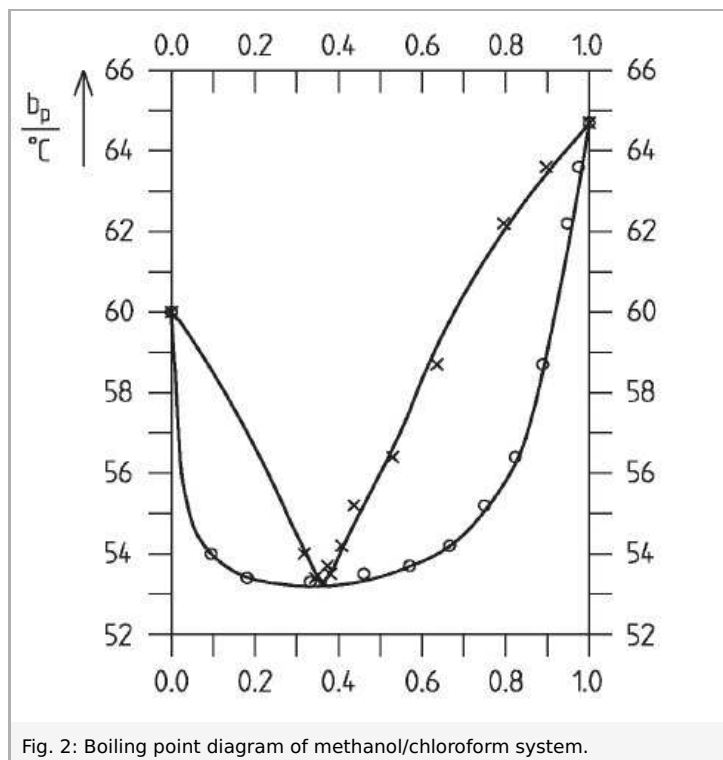
Adjust the heat so that there is a reflux at the protective sleeve for some minutes before the first few drops arrive at the Dimroth cooler. Ensure that only very little of the product distils off so that the composition of the vapour phase does not change. Collect the first drops of the distillate from the distillation head stopcock for measurement of the refractive index and read the boiling point. The refractive index is to be used to determine the composition of the vapour phase from the calibration curve.

After each measurement, pour the mixture out of the flask and clean the apparatus by drawing air through it with the help of the water jet pump. Successively repeat the procedure for all 11 mixtures successively.

Results and evaluation

Results

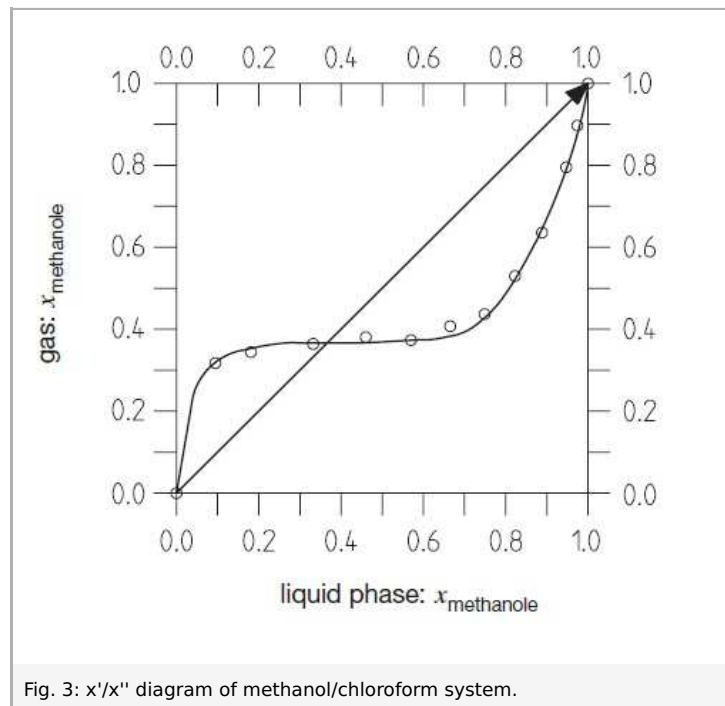
The presentation of the experimentally determined values for the distillation characteristics of methanol / chloroform mixtures is shown in Fig. 2. The system forms an azeotrope at an amount of substance of $x = 0.35$. The compositions of the liquid phase and the vapour phase are identical at this point.



The position of the azeotrope can be determined more exactly by plotting the amount of substance in the liquid phase against that in the vapour phase (Fig. 3). The intersection of this curve with the 45° line gives the composition of the azeotrope.

Literature values:

	Methanol	Chloroform
bp	64.7 °C	61.7 °C
ρ_i^{20}	0.7914 g/cm ³	1.4832 g/cm ³
n_D^{20}	1.3288	1.4459
M	32.04 g/mol	119.38 g/mol



Evaluation

The boiling point diagram graphically depicts the dependence of the boiling point on the composition of the liquid phase at constant pressure. The boiling point curve results from the measurement of the temperatures at which mixtures begin to boil. As the composition of the vapour is as a rule different to that of the liquid, different values are generally obtained for the composition of the condensate to that of the boiling liquid from which it vaporizes (in this experiment, the composition of the vapour phase is determined at the start of boiling for each mixture). The boiling point diagram therefore consists of two curves, the boiling point curve and the condensate curve. The boiling point curve shows the composition of the mixture which begins to boil at a certain temperature, the condensate curve shows the composition of the vapour that is in equilibrium with the liquid mixture at that same temperature.

With an ideal mixture, the boiling point and condensate curves drop continuously with increasing content of the more volatile component. The two curves for the pure components coincide. The mixtures have no constant boiling point, but a boiling interval. Conversion of the total mixture to the vapour phase is only complete when the vapour has the same composition as the liquid phase. Prior to this, the vapour is always enriched with the more volatile liquid.

When a mixture exhibits a maximum vapour pressure, then this corresponds to a minimum boiling point, as the mixture boils quicker the higher the vapour pressure. The boiling point and condensate curves coincide at this maximum point, which indicates that the vapour and the liquid phases have the same composition. On bringing this mixture to boiling, it acts as a pure liquid. Such mixtures, which have a constant boiling point and do not change their composition during boiling, are named azeotropic mixtures.

Plot the measured refractive indices of the pure solvents and eleven mixtures as function of the quantity of substance x_i to obtain the calibration curve (Fig. 4). The quantity of methanol can be derived from

$$x_{\text{methanol}} = \frac{n_{\text{methanol}}}{n_{\text{methanol}} + n_{\text{chloroform}}} \quad (1)$$

The amount of substance of a component i can be obtained from

$$n_i = \frac{V_i \cdot \rho_i}{M_i}$$

where

- V_i Volume of component i
- M_i Molar mass of component i
- ρ_i Density of component i

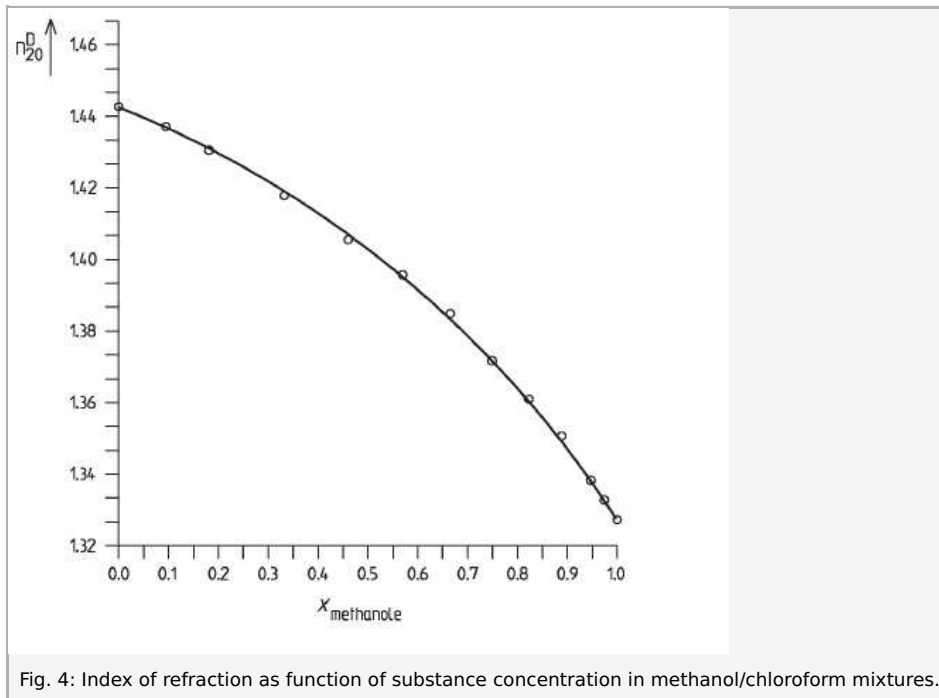


Fig. 4: Index of refraction as function of substance concentration in methanol/chloroform mixtures.

The behaviour of real mixtures cannot be described by the quantity of substance alone, however. The quantity of substance must be multiplied by a correction factor termed the activity coefficient. This reflects the deviation of real solutions from ideal solutions.