GAZİ UNİVERSİTY
CHEMİCAL ENGİNEERİNG DEPARTMENT

CHE 392 CHEMİCAL ENGİNEERİNG LABORATORY I

VAPOR-LIQUID PHASE EQUILIBRIUM(3B)

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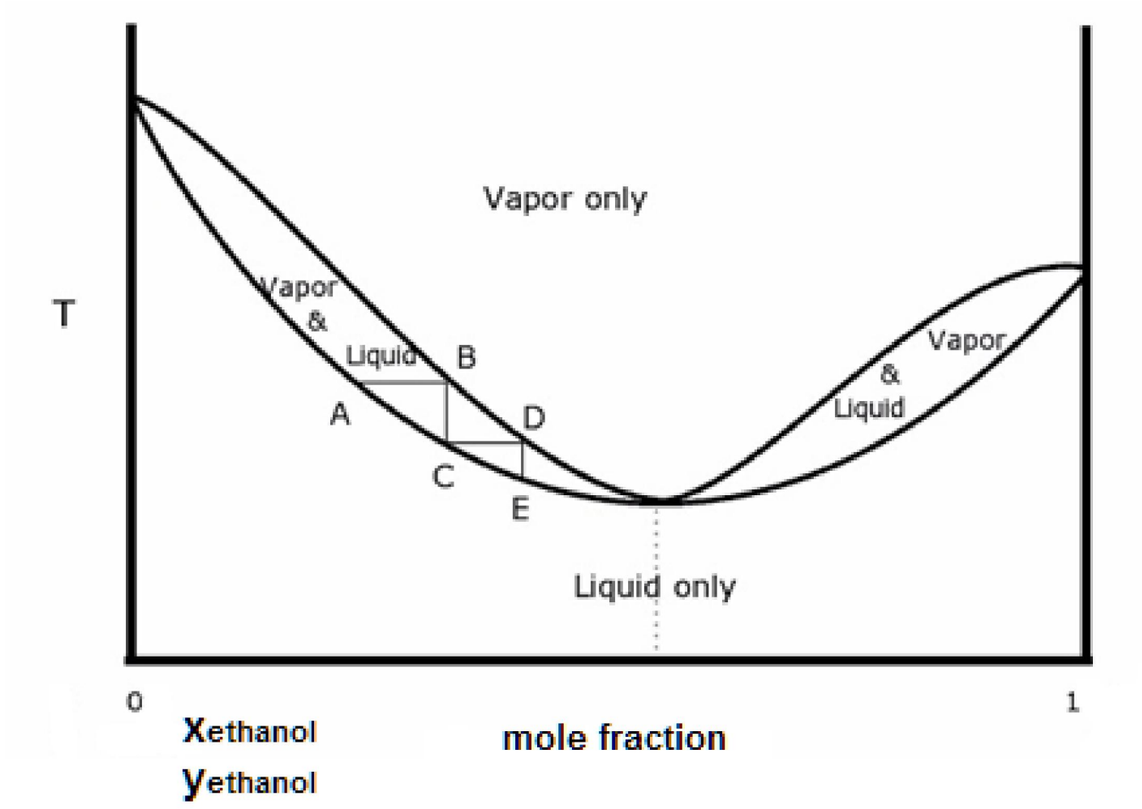
CONTENT

AIM

- The purpose is to obtain a vapor-liquid (temperature-composition, T-$x_{Ethanol}$, $y_{Ethanol}$) phase diagram for a binary system.



PRELIMINARY STUDY

- Refresh your theoretical knowledge of the binary system vapor-liquid phase equilibrium from the relevant sources.
- Discuss the answers to the following questions in the group.
  - Describe ideal and non ideal solutions.
  - Briefly explain Raoult and Henry's laws. In what situations do you argue that they are valid.
  - What is an azeotropic mixture? Qualitatively draw possible phase diagrams for mixtures of this type and discuss the importance of this behavior.
  - What is the phase rule? Please explain. Apply and interpret the phase rule for binary system vapor-liquid phase equilibrium.
  - What is the refractive index? Can you determine the concentration by measuring the refractive index of mixtures? Please explain.

- In this experiment, the vapor-liquid phase equilibrium will be established for the ethanol-water system. In this context, find vapor-liquid equilibrium data given in the literature* for the ethanol water system and draw the T-$x_{Ethanol}$, $y_{Ethanol}$ equilibrium diagram.
- The refractometer available in the laboratory can be used for concentration measurements. In this context, depending on the mole fraction of the ethanol-water mixture, the refractive index is found in the literature*.
- The refractive index values of the ethanol-water mixture from the literature can be measured using a refractometer at several points. if these values deviate more than the values given in the literature, discuss how to follow a method for reasons.
- Observe the safety data sheets (MSDS) of the used chemicals and take the necessary precautions

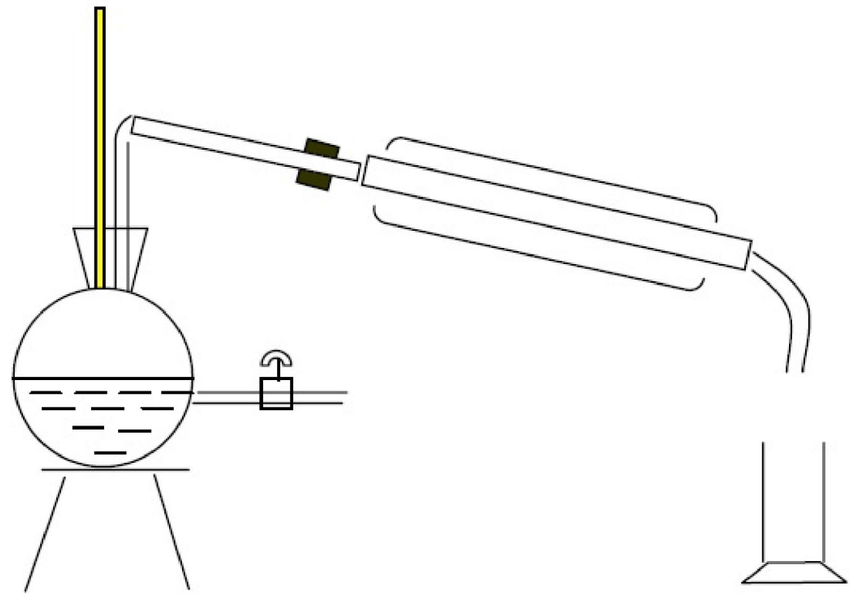
*The theoretical data required for the ethanol-water system is given in the appendix.

EXPERIMENTAL WORK

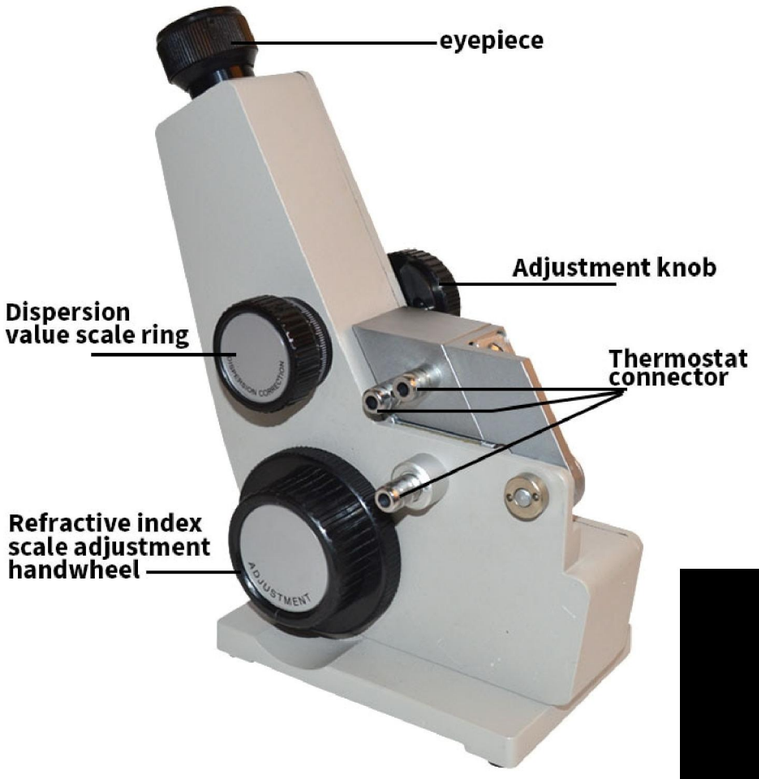
- Ethanol-water mixture will be used for the vapor-liquid phase balance. The experiment consists of two stages.
  - 1) To create the calibration curve by measuring the refractive indexes of ethanol-water volume
    - **Calibration graph will be drawn refractive index versus mole fraction of ethanol**
  - 2) Measurement of refractive indexes against temperature by distillation of 75% ethanol-water mixture

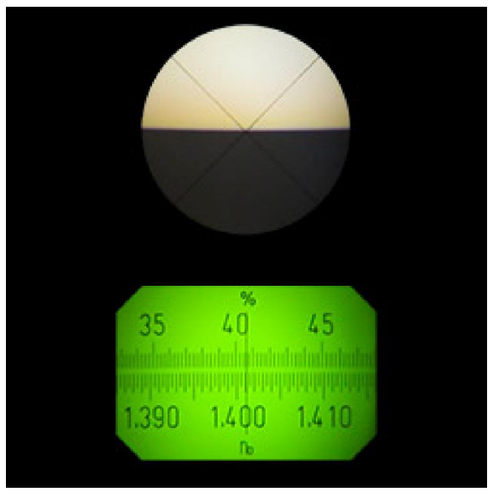
Experimental setup, materials and chemicals to be used

- Three necks round-bottom flasks
- Cooler and cooling water connections
- Heater
- Refractometer
- Beaker, test tube, pipette, tissue paper
- Tap to provide cooling water
- Ethanol solution
- Pure water



Refractive index measurement





- 1) Take the device carefully from the box.
- 2) The lamps are mounted on the appliance and check that they are in working condition.
- 3) The sample place is opened and wiped clean with a dry cloth or napkin. This process is repeated before every measurement.
- 4) After 1-2 drops of sample have been placed, the sample place is closed.
- 5) Looking at the ocular, first the sharpness of the thick line seen in the upper part is adjusted with the small adjustment knob located on the right side of the device.
- 6)Once the sharpness setting is done, using the big button on the right side of the device, the thick line is brought to the center of the ⧖ symbol. Then, on the scale shown below, the value is read and recorded. The ocular viewer should see half of a circle black and half bright and the separation boundary of these two half circles must be sharp.
- 7) After the measurements are completed, the lamps on the device are first removed and the device is cleaned and placed in its box.

I)Study for the calibration curve

- Ethanol-water solution of 10%, 20%, ... 90% by volume is prepared and refractive indexes are measured and recorded with a refractometer.
- Total solution volume is 10 ml;
  - 0% ethanol → 10ml pure water
  - 10% ethanol → 1ml ethanol 9ml pure water…
- The calibration curve is prepared by plotting the refractive index versus the mole fraction of ethanol.

$$x_{\text{Ethanol}} = \frac{n_{\text{Ethanol}}}{n_{\text{Ethanol}} + n_{water}}$$

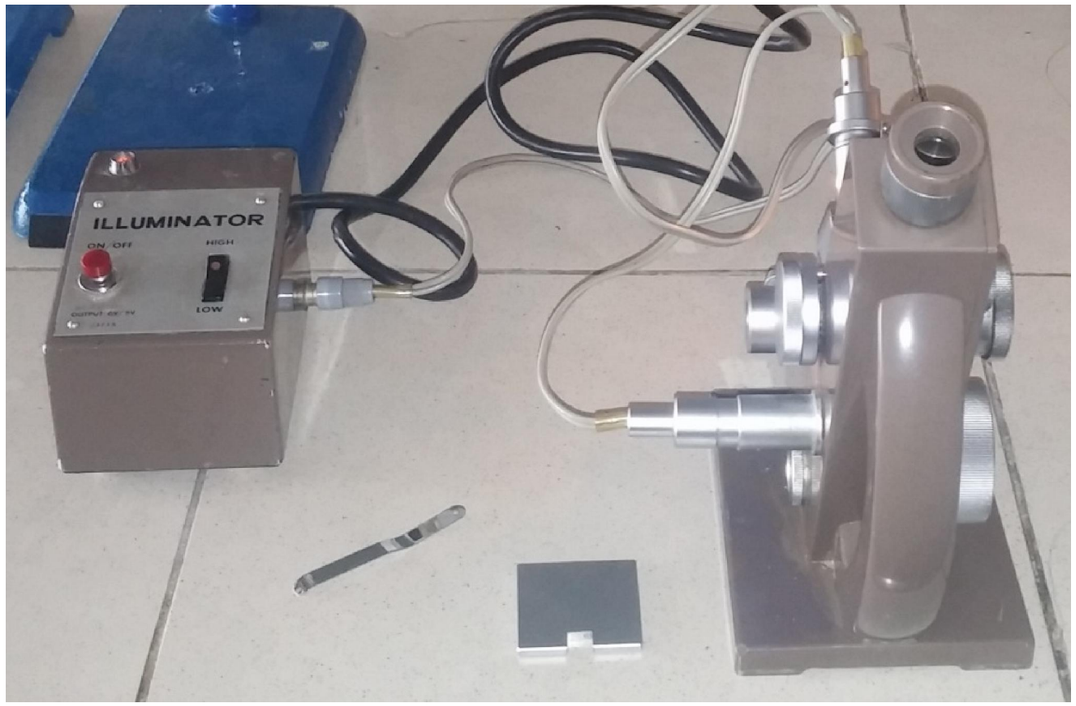
Table 1. Refractive index values of ethanol-water mixtures prepared in different volume percentages

Ethanol-water solution % (by volume)	Refractive index values
0	1.3316
10	1.3395
20	1.3464
30	1.3522
40	1.3577
50	1.3607
60	1.3632
70	1.3644
80	1.3648
90	1.3640
100	1.3614

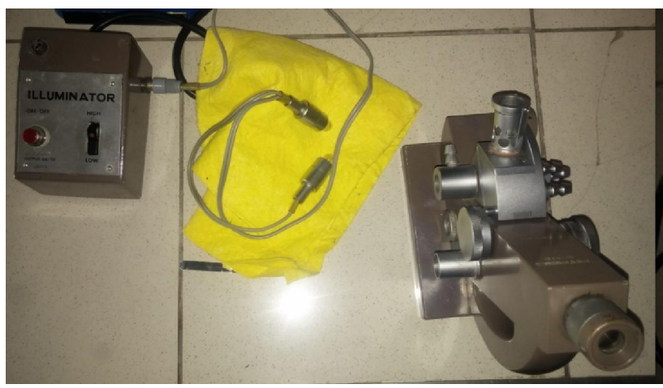
II) Vapor-liquid phase equilibrium experiment

- 75% ethanol-water solution is taken into the simple distillation system and the temperature is set. With the first distillate removal, the temperature is increased 1-2°C regularly. Temperature ranges from 78-100°C approximately.
- Along with the first distillate, samples are taken from the distillate (vapor phase, $y_{Ethanol}$) and the mixture in the flask (liquid phase, $x_{Ethanol}$) with the help of a pipette. Immediately afterwards, refractive indexes are measured with a refractometer and the data are saved against temperature.

Experimental setup and functions;
balloon is covered with balloon jacket heater. On the right side of the 3-necked balloon, a thermometer is kept in contact with the steam, the left side is used for sampling, it consists of a back-cooler cooled by tap water and a container in which the distillate accumulates.



The lamps of the refractometer are first removed and after 1-2 drops of sample are dropped into the prism chamber, the lamps are put back and the refractive index is measured after looking through the eyepieces (Slide 8).



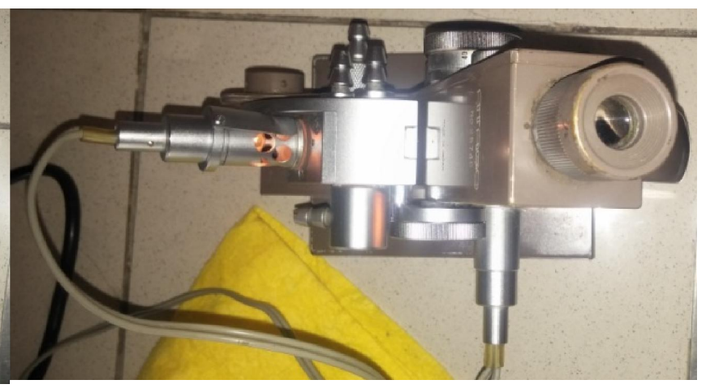


Table 2. Liquid and vapor phase experimental refractive index data of 75% ethanol-water mixture

Temperature,°C	Liquid phase refractive index	Vapor phase refractive index
79	1.3706	1.3704
80	1.3692	1.3704
81	1.3686	1.3702
82	1.3675	1.3701
84	1.3663	1.3692
85	1.3654	1.3684
87	1.3627	1.3684
90	1.3584	1.3663
96	1.3518	1.3564
100	1.3478	1.3478

EVALUATION OF DATA

- 1) With the help of data, create T-$x_{Ethanol}$, $y_{Ethanol}$ diagram. Compare the diagram generated from experimental data with the literature.
- 2) Try to calculate the theoretical liquid phase compositions using the experimental vapor phase curve and the theoretical vapor phase compositions using the experimental liquid phase curve. Do not forget to mention clearly your assumptions.
- 3) Plot T versus $y_{Ethanol}$ -$x_{Ethanol}$ (vapor phase mole fraction - liquid phase mole fraction) curve.

Calculation Method

- From the Antoine equation, the pure vapor pressure (P°) of ethanol against the temperature is obtained.

$$\log P = A - \frac{B}{C + T}$$

- Antoine constants for ethanol (T=77-243°C)(T[=]°C; P[=] mmHg)
  - A=7,68117; B=1332,04; C=199,200
- From the composition of the vapor in equilibrium with the liquid at temperature T; Theoretical liquid phase is calculated from the experimental vapor phase data and theoretical liquid phase is calculated from the experimental liquid phase data.(*Examine the Raoult's law, liquid-gas equilibrium, the equilibrium between phases*)

$$P^{o}_{\text{etanol}} \times x_{\text{etanol}} = P_T \times y_{\text{etanol}}$$

REFERANCES

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- GEANKOPLIS, C., J.,*Transport processes and separation process principles:(includes unit operations)*, Prentice Hall Professional Technical Reference, 2003.
- YALÇIN, H., ve GÜRÜ, M., Mühendislik Termodinamiği, Palme Yayıncılık, 2. Baskı, 2004.
- UYSAL, B., Z., Kütle Transferi Esasları ve Uygulamaları, Gazi Üniversitesi, 1996.
- Cazes, J. (Ed.), *Analytical instrumentation handbook*, CRC Press, 2004.

APPENDIXS: Equilibrium data for ethanol-water system at 1 atm

Tempreture (ºC)	$x_{Ethanol}$ (liquid phase mole fraction)	$y_{Ethanol}$ (vapor phase mole fraction)
100	0	0
95.5	0.019	0.17
89	0.0721	0.3891
86.7	0.0966	0.4375
85.3	0.1238	0.4704
84.1	0.1661	0.5089
82.7	0.2337	0.5445
82.3	0.2608	0.558
81.5	0.3273	0.5826
80.7	0.3965	0.6122
79.8	0.5079	0.6564
79.7	0.5198	0.6599
79.3	0.5732	0.6841
78.7	0.6763	0.7385
78.4	0.7472	0.7815
78.1	0.8943	0.8943

GEANKOPLIS, C., J.,*Transport processes and separation process principles:(includes unit operations)*, Prentice Hall Professional Technical Reference, 2003.

Refractive indexes of ethanol solution at 20°C

Concentration (by mass %)	(n) Refractive index
0	1.3330
2	1.3342
4	1.3354
6	1.3367
8	1.3381
10	1.3395
12	1.3410
14	1.3425
16	1.3440
18	1.3455
20	1.3469
22	1.3484
26	1.3511
28	1.3524
30	1.3535
32	1.3546
34	1.3557
36	1.3566
38	1.3575
40	1.3583
42	1.3590
44	1.3598
46	1.3604
48	1.3610
50	1.3616
52	1.3621
54	1.3626
56	1.3630
58	1.3634
60	1.3638
62	1.3641
64	1.3644
66	1.3647
68	1.3650
70	1.3652
72	1.3654
74	1.3655
76	1.3657
78	1.3657
80	1.3658
82	1.3657
84	1.3656
86	1.3655
88	1.3653
90	1.3650
92	1.3646
94	1.3642
96	1.3636
98	1.3630
100	1.3614

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