

Isobaric Vapour-Liquid Equilibrium of Binary Mixture of 1, 2-Di-chloroethane with 1-Heptanol at 95.72 Kpa

Sai kumar Bitta
Department Of Chemical
Engineering
Chaitanya Bharathi Institute of
Technology
Gandipet, Hyderabad 500075,
INDIA

Guide: Mr. V. Ananth Kumar
Thimmarusu
Associate Professor Department Of
Chemical Engineering, Chaitanya
Bharathi Institute of Technology,
Gandipet, Hyderabad 500075,
INDIA

B. Varsha Goud
Department Of Chemical
Engineering
Chaitanya Bharathi Institute of
Technology
Gandipet, Hyderabad 500075,
INDIA

Abstract— Experimentally the isobaric vapor-liquid equilibrium (VLE) data for the binary system (1,2-Dichloroethane + 1-Heptanol) is found at pressure (720mm Hg) at varied mole fractions. The measurements have been performed using a vapor recirculating type (Swietoslawski ebulliometer) equilibrium still. The mixture shows positive deviation from ideality and does not form an azeotrope. The activity coefficients of the system were correlated with the Van Laar model. The relationship of the liquid composition (X_1) as a function of temperature (T) was found to be well represented by the Van Laar Model. The results showed that the calculated values of the vapor phase mole fraction and boiling temperature are agreed well with the experimental data. Furthermore, the VLE data shown to be thermodynamically consistent and is determined by Herington Test. The calculations are done for Antoine constants to find vapour pressures, Van Laar equation to find the activity coefficients, excess Gibbs free energy. Vapour liquid equilibrium measurements are carried out for binary mixtures based on their industrial importance in chemical engineering separation operation and strongly non ideal behavior.

Keywords: 1) SWIETOSLAWKI Ebulliometer, 2) Binary mixture, 3) Vapor-liquid equilibrium, 4) 1-Heptanol

I. INTRODUCTION

The measurement, modeling and computation of phase equilibria have been one of the most compelling problems of chemical engineering. The variety of experimental and computational methods developed by chemical engineers and physical chemists for measurement and thermodynamic interpretation of vapor-liquid equilibria

(VLE) probably surpasses all other areas of chemical engineering research. The VLE information is useful in designing separation processes such as distillation, adsorption, stripping and liquid-liquid extraction, which are major components of industrial processes involving hydrocarbons, and their cost frequently represents a major fraction of total plant cost. Also the VLE studies have

assumed greater importance with the expansion of petrochemical industry and the fast increase in number of pure components that are required to be distilled

Very limited work has been reported on vapor-liquid equilibrium study of binary mixtures containing 1-Heptanol as one of the component. Such components form industrially important combinations in petroleum and petrochemical industries. In view of their close boiling point and varied binary interactions, separation becomes difficult. For the rigorous simulation and optimization of the separation of C_9 aromatic compounds, an accurate description of vapor-liquid equilibria is required.

As part of a wide experimental and theoretical study on thermodynamic and physicochemical properties of binary liquid mixtures containing C_9 aromatic compounds and linear alcohols, and with the aim of studying in depth, the behavior of these kinds of mixtures, we are reporting experimental vapor-liquid equilibrium data for binary mixture of 1-Heptanol (H) and 1, 2-Dichloroethane(DE). The measurements were performed under isobaric conditions at a pressure of 95.72 kPa using a modified version of the recirculating type equilibrium still i.e. SWIETOSLAWKI type ebulliometer.

II. EASE OF USE

A. Industrial uses of this binary mixtures

Heptan-1-ol (CAS RN:111-70-6) has a pleasant smell and is used in cosmetics for its fragrance. Pure 1, 2-dichloroethane (CAS RN: 107-06-2) find its application in many pharmaceutical and chemical industries as the primary solvent, and for resins and cellulose esters. In addition to above-mentioned applications, the mixture of these alcohols find uses in solubilization (reaction medium), extraction, and crystallization of active pharmaceutical ingredients.

B. Materials

The reagents Heptanol-1, and 1, 2-Dichloroethane are purchased from Sigma-Aldrich Chemicals Pvt.

Limited, India. The purities of the reagents are confirmed by gas chromatography with more than 0.99 mass fraction.

III. METHODS FOR DETERMINATION OF VAPOUR LIQUID EQUILIBRIUM

There are relatively few ideal system whose equilibrium relations can be calculated using Raoult's law and Dalton's law (i.e. from the known dependency of the vapour pressure of the pure constituents on temperature). On the other hand there are large numbers of industrially important systems whose equilibrium relations cannot be predicted from purely theoretical considerations of the both the phases analytically. The direct experimental determinations of vapour liquid equilibria require sampling of the liquid vapour, which are in thermodynamic equilibrium and determining the contacting of solutions.

The methods for experimental determination of vapour-liquid-equilibria are classified into the following groups.

- Static method
- Distillation and Circulation method
- Dew and Bubble point method
- Flow method

Distillation and circulation is direct method for the experimental determination of vapour- liquid-equilibria data.

A. Apparatus for the estimation of vapour liquid equilibria:

The apparatus used for the determination of vapour liquid equilibria is called EBULLIOMETER.

There are different types of ebulliometers:

- Cottrell ebulliometer
- Washburn ebulliometer
- Swietoslowski ebulliometer

The name ebulliometer has its roots in the Latin word "ebullio": meaning to boil or bubble up. An ebulliometer is designed to accurately measure the boiling point (temperature) of water or a water solution, by measuring the temperature of the vapour generated away from the heat source.

An ebulliometer is designed to accurately measure the boiling point of liquids by measuring the temperature of the vapor-liquid equilibrium either isobarically or isothermally. The method of using a vessel containing boiling substance into which the thermometer is immersed is not accurate. The boiling point measured by placing a thermometer in the boiling liquid above the vapour is not the actual boiling point.

For example, a small amount of water may cause a large deviation of the condensation temperature from boiling point, COTTRELL and WASHBURN simultaneously published a method for this measurement of the boiling point of the liquid it was possible to determine the boiling point of liquid so accurately.

B Equipment used:

The equipment we used is SWIETOSLAWKI type ebulliometer is very similar to the one described by Halaetal (1958) was used for the experiments. One end of this ebulliometer was kept open so as to carry out experiment under a constant pressure equal to the atmospheric pressure.

The thermometer bulb is located at the point in a thermo well filled with silicon oil where the gas liquid mixture impinges. The mixture samples to be studied are prepared by weighing the required amount of the pure liquids and stirring them well before charging them to the still. The heating rate is adjusted to yield the desired drop rate of about 30drops per minute [in accordance with suggestion of Hala(1958)]. The equilibrium temperature is recorded after steady state conditions judged by the constant temperature and uniform drop rate for at least 30 drops per minute.

SKETCH OF EBULLIOMETER

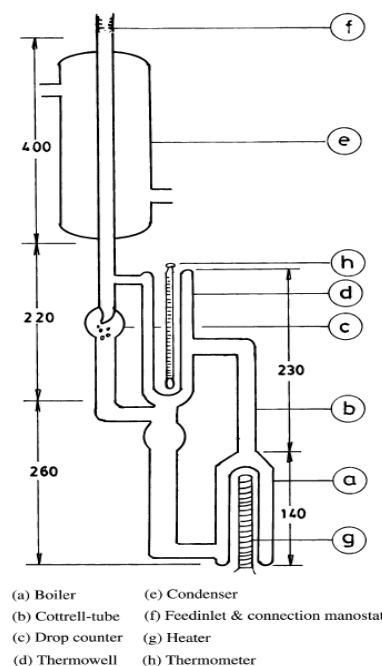


Fig. 1. Swietoslowski ebulliometer.

Figure-1

An ebulliometer apparatus consists of-

1. A chamber to hold the liquid whose boiling point is to be determined and is designed to allow for a semi-remote heat source.
2. A condenser (reflux) to continually condense the vapour generated, to maintain the initial concentration of the liquid being tested.
3. A special, precision thermometer calibrated in 0.02°C with a range of 35-250°C
4. A heat source such as a heater.
5. An outlet tap to allow removal of rinsing or tested liquid. A dedicated measuring cylinder marked at a 50ml volume.

B. Experimental Determination Of Vapour Liquid Equilibria

The test mixtures, in desired compositions were prepared gravimetrically using an electronic balance precise to ± 0.0001 g. The prepared mixture was stirred well and charged to the ebulliometer and heated by gradually increasing the heat supply. The equilibrium state was observed by drop count of 30 per minute. The boiling point was ascertained by constancy of temperature for about 30 min. At this steady state, the temperature was noted by using a calibrated mercury thermometer (accurate to ± 1 K), and the samples withdrawn and analyzed.

IV. CALCULATIONS

A. Mole fraction or composition (X_1):-

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The given equation is used for calculation the mole fraction of given solution.

1,2-Dichloromethane(DE) + 1-Heptanol(H).

$$X_1 = \{[W_1/M_1]/[(W_1/M_1)+(W_2/M_2)]\} \quad (1)$$

Where W_1 is weight, V_1 is volume, ρ_1 is density, X_1 is the mole fraction and M_1 is molar mass of low boiling substance i.e. 1, 2 Dichloroethane (DE) and W_2 is weight, V_2 is volume, ρ_2 is density, X_2 is the mole fraction and M_2 is molar mass of high boiling substance i.e. 1-Heptanol (H).

Low boiling substance (DE):

High boiling substance (H):

$$\begin{aligned} V_1 &= 5\text{ml}, \rho_1 = 1.168 \text{ and } V_2 = 48 \text{ ml}, \\ \rho_2 &= 0.822 \text{ and } M_1 = 98.96, M_2 = 116. \\ X_1 &= \{[5 * 1.168 / 98.96] / [(5 * 1.168 / 98.96) + (48 \\ &\quad * 0.822 / 116.204)]\} \\ &= 0.0590 / 0.0590 + 0.3985 \\ *X_1 &= 0.1478 \\ X_2 &= 1 - X_1 \quad (2) \\ 1 - 0.1478 &= 0.852 \\ *X_1 = 0.1478 &\quad *X_2 = 0.852 \end{aligned}$$

B. Calculation of saturated vapour pressure (P^l_s, P^2_s):

Calculation of saturated vapour pressures using Antoine Equation.

The equation is given by

$$\ln(p^1) = A - [B/T(K) + C] \quad (3)$$

Where A, B and C are Antoine Constant and T(K) is temperature in Kelvin.

□ Antoine Constants are taken from property Data bank.

Antoine constants for 1, 2-dichloroethane is

Low boiling substance (DE):

$$A = 16.1764, B = 2927.17, C = -50.22$$

Antoine constants for 1-heptanol is

High boiling substance (H):

$$\begin{aligned} A &= 15.3068, B = 2626.42, C = -146.6 \\ \ln(P^1_s) &= 16.1764 - [2927.17 / 416.15 - 50.22] \\ \ln(P^2_s) &= 15.3068 - [2626.42 / 416.15 - 146.6] \\ &\bullet P^1_s = 3558.65 \text{ mmHg.} \\ &\bullet P^2_s = 260.624 \text{ mmHg.} \end{aligned}$$

C. calculation of Activity coefficients (γ_1, γ_2)

Calculation of activity coefficients by using Vanlaar equation, given by

$$RT(K) \ln \gamma_i = A_i [1 + (A_i X_i / B_i X_2)]^{-2} \quad (4)$$

Where R is ideal gas constant

$$A_i = M_1 / \rho_1 \text{ and } B_i = M_2 / \rho_2$$

$$R = 1.987 \text{ (Kcal/Kmol. K)}, T = 416.15 \text{ K}, A_1 = 84.726 \text{ and } B_1 = 141.367$$

$$1.987 * 416.15 \ln \gamma_1 =$$

$$84.726 * [1 + (84.726 * 0.148 / 141.367 * 0.8514)]^{-2}$$

$$826.890 \ln \gamma_1 = 84.726 [1 + 0.1046]^{-2}$$

$$826.890 \ln \gamma_1 = 69.4342$$

$$\ln \gamma_1 = 69.4342 / 826.890$$

$$\bullet \gamma_1 = 1.0874$$

Similarly γ_2

$$R T (K) \ln \gamma_2 = B_1 [1 + (B_1 X_2 / A_1 X_1)]^{-2} \quad (5)$$

$$\bullet \gamma_2 = 1.0011$$

D. Calculation of Excess Gibb's free energy (G^E):

$$G^E = RT (K) [X_1 \ln \gamma_1 + X_2 \ln \gamma_2] \quad (6)$$

$$= 826.89 * [0.1486 * 0.0839 + 0.8514 * (1.5341 * 10^{-3})]$$

$$\bullet G^E = 11.0769$$

| X_1 | T_k | P_s^1 | P_s^2 | γ_1 | γ_2 | $\log\gamma_1/\gamma_2$ | Y_1 | G^E |
|--------|--------|---------|---------|------------|------------|-------------------------|--------|--------|
| 0.0715 | 424.15 | 4222.89 | 395.593 | 1.0962 | 1.0003 | 0.0397 | 0.0826 | 5.7872 |
| 0.1486 | 416.15 | 3558.65 | 260.624 | 1.0875 | 1.0015 | 0.0357 | 0.7212 | 11.333 |
| 0.2101 | 406.15 | 2842.37 | 179.051 | 1.0812 | 1.0033 | 0.0324 | 0.8081 | 15.353 |
| 0.2579 | 403.15 | 2650.46 | 159.069 | 1.0751 | 1.0052 | 0.0291 | 0.8609 | 18.017 |
| 0.3395 | 391.15 | 1979.42 | 96.2591 | 1.0657 | 1.0105 | 0.0230 | 0.9176 | 22.120 |
| 0.4100 | 384.15 | 1653.38 | 70.1416 | 1.0568 | 1.0161 | 0.017 | 0.944 | 24.455 |
| 0.4649 | 381.15 | 1527.08 | 60.8918 | 1.0495 | 1.0221 | 0.0149 | 0.9572 | 25.799 |
| 0.5601 | 378.15 | 1408.38 | 52.6687 | 1.0369 | 1.0018 | 0.0149 | 0.9572 | 15.790 |
| 0.6612 | 376.15 | 1333.13 | 61.5724 | 1.0243 | 1.0565 | -0.013 | 0.9724 | 26.084 |
| 0.7621 | 374.15 | 1261.39 | 43.1478 | 1.0134 | 1.0856 | -0.029 | 0.9886 | 22.046 |
| 0.8002 | 368.15 | 1063.69 | 31.565 | 1.0 | 1.1012 | -0.037 | 0.992 | 19.918 |
| 0.8890 | 365.15 | 974.311 | 26.8246 | 1.0 | 1.1464 | -0.057 | 0.996 | 13.378 |
| 0.9412 | 362.15 | 890.99 | 22.6931 | 1.0 | 1.1748 | -0.069 | 0.9983 | 6.8454 |
| 1.000 | 355.15 | 718.322 | 15.075 | 1.1275 | 1.2218 | -0.348 | 1 | 84.689 |

Table: 1 calculation of 1,2 – Dichloroethane (DE) + 1 – Heptanol (H)

D. Graphs

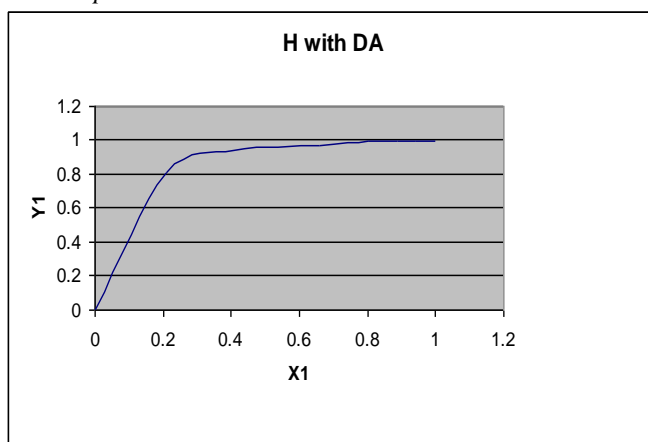


Figure 2

This graph shows the comparison between the liquid composition (X_1) and vapor composition (Y_1) of binary mixture DE + H.

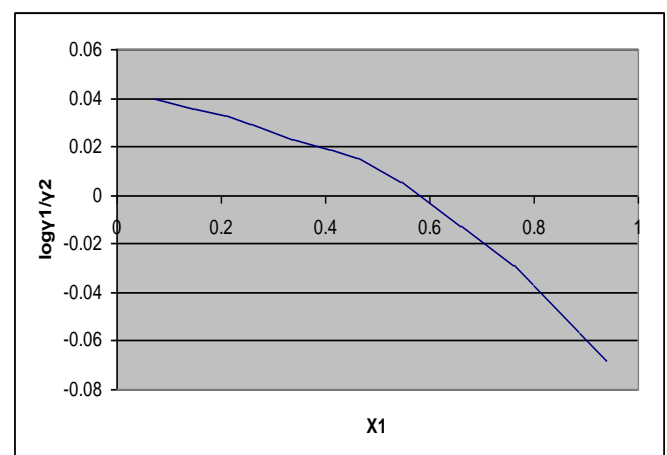


Figure 3

This graph shows the comparison between the liquid composition (X_1) and activity coefficients ($\log \gamma_1 / \gamma_2$) of binary mixture DE + H.

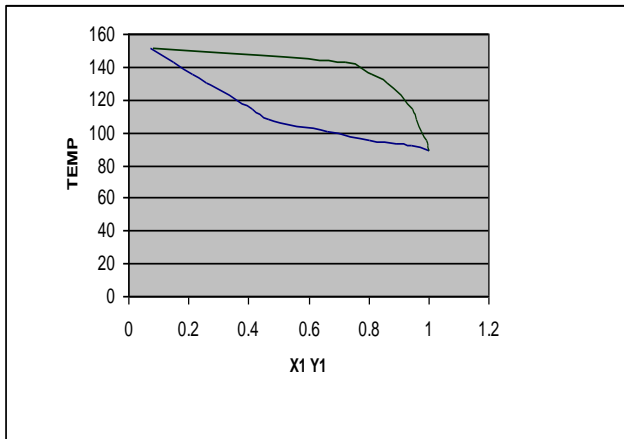


Figure 4

This graph shows the comparison between the liquid (X1) and vapor (Y1) composition with temperature (T) of binary mixture DE + H.

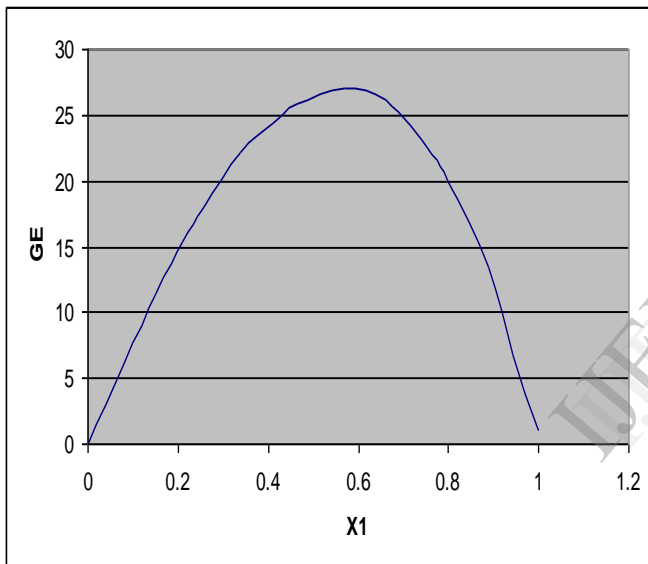


Figure 5

This graph shows the comparison between the liquid composition (X1) and Excess Gibbs Free energy (G^E) of binary mixture DE + H.

V. RESULTS AND DISCUSSIONS:

Vapour liquid equilibrium measurements are carried out for one binary mixture based on its industrial importance in chemical engineering separation operation and strongly non ideal behavior.

A thorough literature research has been conducted and revealed that no information is available for this system. Temperature-composition measurements are carried out at atmospheric pressures i.e. 716 mmHg or 718 mmHg. The calculations are done for Antoine constants to find vapour pressures, Vanlaar equation to find the activity coefficients, excess gibbs free energy.

Discussions:

Consistency of experimental values is determined by using HERINGTON TEST.

(area above X-axis – area below Y-axis)

/(area above X-axis + area below Y-axis)

≤ 0.02 .

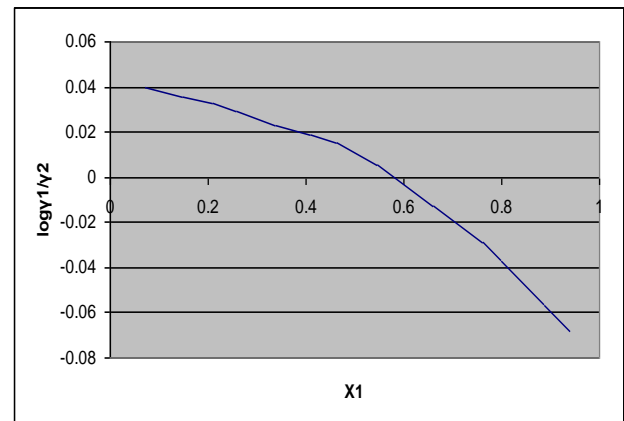
Graph of $\log \gamma^1/\gamma^2$ vs x_1 

Figure 6

Consistency Test:

$$(0.011 - 0.044) / (0.011 + 0.044) = -0.6 \leq 0.02.$$

Therefore value obtained by the above test is found to be true.

VI. REFERENCES

- [1] Distillation by Van Winkle
- [2] Encyclopedia of chemical technology, fifth edition, volume-2; Author Kirk-othmer.
- [3] Encyclopedia of science and technology, sixth edition, volume 1, 7; Author: Graw Hill.
- [4] Encyclopedia of Industrial chemistry, fifth edition, volume -9; Author: Ullmann's.
- [5] Mass Transfer Operations by Robert E. Treybal.
- [6] T.E. Vittal Prasad, A.Sravan Kumar, D.H.L. Prasad; Fluid Phase Equilibria: 201, (2002), 47-55
- [7] J.A. Riddick, W.S. Bunger, T.K. Sakno;
- [8] Organic Solvents: physical properties and methods of purification; Vol-2, fourth edition, New York, 1986.
- [9] Journals of Chemical & Thermodynamic
- [10] Journals of Chemical & Fluid Phase Equilibria.
- [11] Properties of Liquids and Gases by Reid & Sherwood.