

**An-Najah National University**  
**Faculty of Graduate Studies**

**Critical Behavior of the Density  
of Binary Liquid Mixture  
Cyclohexane – Phenol**

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**This Thesis is Submitted in Partial Fulfillment of the Requirements for  
the Degree of Master of Physics, Faculty of Graduate Studies, An-  
Najah National University - Nablus, Palestine.**

**2015**

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Liquid Mixture Cyclohexane – Phenol**

**By**

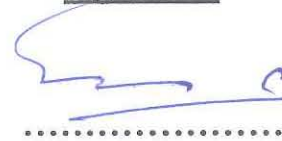
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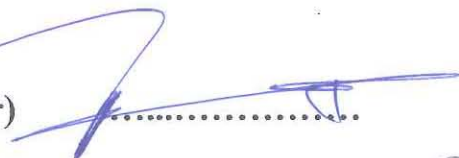
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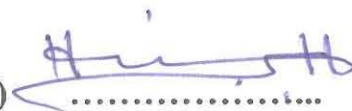
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### III

#### **Dedication**

*This thesis is dedicated to the candles that were burned yesterday to light up my life today, my father and mother.*

### **Acknowledgement**

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## الإقرار

أنا الموقعة أدناه مقدمة الرسالة التي تحمل العنوان:

## Critical Behavior of the Density of Binary Liquid Mixture Cyclohexane – Phenol

أقر بان ما اشتملت عليه هذه الرسالة إنما هو نتاج جهدي الخاص ، باستثناء ما تمت الإشارة إليه  
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### Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

Student's name: Ghadeer Hussien. اسم الطالب:

Signature: Ghadeer التوقيع:

Date: 1/4/2015 التاريخ:

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X  
**Critical Behavior of the Density of Binary Liquid Mixture  
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**Dr. Iyad Saadeddin**

**Abstract**

The dynamic shear viscosity coefficients of the binary liquid mixture cyclohexane-phenol for different phenol concentrations and temperatures are measured using glass capillary viscometer. Dynamic shear viscosity anomaly is observed near the critical temperature  $T_c = 17.0^\circ\text{C}$  and the critical concentration of phenol  $x_c = 2.70\%$  by weight. Mode Coupling Theory is used to fit our experimental data above the critical temperature. It is found that the value of noncritical part of the dynamic shear viscosity  $\eta_0 = 0.8174$  cP. The power law is expected for the mass density above critical temperature. The value of noncritical part of the mass density is found to be  $\rho_0 = 0.7357 \frac{\text{gm}}{\text{cm}^3}$ . The critical isobaric thermal expansion coefficient  $\alpha_{pc}$  was calculated to be  $1.66 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ . The critical isobaric specific heat  $c_{pc}$  was found to be  $106.6 \frac{\text{Joule}}{\text{kg.K}}$ . Joule's constant  $J$  was found to be  $4.1180 \frac{\text{Calorie}}{\text{Joule}}$  and pressure derivation of the critical temperature  $T_c'$  was also calculated to be  $1.22 \times 10^{-4} \frac{\text{K}}{\text{Pa}}$ .

## Chapter One

### Introduction

#### 1.1 Liquids and Binary Mixtures

The liquid state of matter is intuitively perceived as being intermediate in nature between gas and solid. Thus, a natural starting point for discussion of the properties of any given substance is the relationship between pressure  $P$ , density  $\rho$  and temperature  $T$  in the different phases (Hansen and McDonald, 2005).

Binary mixture is a mixture that contains two different liquids; it has definition at a critical temperature and critical concentration, where the mixture mixes homogeneously. The two components do not mix homogeneously in all proportions below this temperature, and can define two different phases. Examples of binary mixtures are benzene - coconut oil, nitrobenzene - n-hexane, and methanol - cyclohexane (Abdelraziq, 2005; Bsharat, 2015).

The existence of critical point affects the physicochemical properties of the system in the stable liquid phase and is the reason for anomalous behavior of many physical quantities sensitive to the in homogeneity of the medium (Ratajczak *et al*, 2010). The locus of the critical point represents the boundary between regions of homogeneous and heterogeneous behaviour in phase diagrams for mixtures (Laura *et al*, 2008).

The studies of excess properties such as deviation in viscosity, excess molar volume, excess Gibbs free energy of activation of viscous flow and

Grunberg-Nissan interaction constant of binary mixtures are useful in understanding the nature of intermolecular interactions between two liquids. Properties such as density and viscosity at several temperatures for binary liquid mixtures over the whole composition range are useful for understanding of the thermodynamic and transport properties associated with heat and fluid flow (Ezekiel *et al*, 2012).

## 1.2 Literature Review

The first attempt to understand the behavior of the shear viscosity in the critical region of a binary liquid system goes back to Fixman. His approach had some serious drawbacks (Fixman, 1962).

Wei - Kuan studied the isothermal vapor - liquid equilibrium at 333.15K and 353.15 K and density measurement for four binary mixture of benzene + nonane, toluene + o-xylene, m-xylene + sulfolane and o-xylene + sulfolane at pressures from 0 Pa to 101.3 kPa. Experimental data of phase densities were measured using the bubble – point method couple with two vibration densitometers. The calculated activity coefficient, excess molar volume and excess Gibbs energy values detected that the toluene + o-xylene was close to the ideal solution (Wei - Kuan *et al*, 2010).

Laura studied the critical properties of pure and binary mixture of liquid solvent CO<sub>2</sub> + ethane as a function of pressure and temperature. The critical location of CO<sub>2</sub> + ethane binary mixture has been measured at mole fraction  $x_c = 0.5$ ,  $T_c = 308.15$  K and pressures up to  $200 \times 10^5$  Pa. (Laura *et al*, 2012).

Jian - Ying determined the density and surface tension of pure ionic liquid and its binary mixtures with water have measured as function of temperature at constant pressure. The thermal expansion coefficient was determined using the experimental density result. The density values decreased when temperature increased, and it also decreased by increasing the mole fraction and the molar volumes of binary mixture were positive in the whole composition range (Jian - Ying *et al*, 2011).

Domanska and Krolikowska measured the densities and viscosities correlations for five different binary mixtures of the ionic liquids (Domanska and Krolikowska, 2012). The tracer diffusion coefficients of the binary mixture like tritiated water and acetonitrile in water - acetonitrile have been measured at several temperatures (Easteal, 1980).

The measurements of the saturated liquid and vapor densities were made for binary mixtures in critical region. The vapor-liquid coexistence curves were obtained for three different compositions by observations of the critical temperatures, critical densities and critical molar volumes (Ryo *et al*, 2013).

Zhang and his group measured density of the binary system of poly(ethylene glycol) 300 (PEG 300) + water over the whole concentration range at five temperatures from (298.15 to 318.15) K. The density was fitted to calculate the excess molar volume and viscosity deviation. The values of the excess molar volume for all mixtures were negative, while the values of viscosity deviation were positive over the entire composition range (Zhang *et al*, 2012).

Juntarachat and his group measured critical properties for the binary mixtures composed of carbon dioxide and n-alkanes ( $\text{CO}_2$  + n-pentane,  $\text{CO}_2$  + n-heptane and  $\text{CO}_2$  + n-decane) critical temperatures ( $T_c$ ) and critical pressures ( $P_c$ ) are measured. The critical points are visually measured by observing the critical opalescence and the simultaneous disappearance and reappearance of the convex surface in the middle of the view cell which withstands operations up to 673 K and 20 MPa (Juntarachat *et al*, 2012).

The heat capacity of the liquid–liquid mixture isobutyric acid–water has been measured for the first time near and far away from its critical point using an adiabatic calorimeter. The measurements were performed at atmospheric pressure, in the first phase region as a function of three temperatures:  $T - T_c = 0.055$  °C,  $T - T_c = 3.055$  °C,  $T - T_c = 8.055$  °C and of the composition mass fraction of the isobutyric acid. The heat capacity at constant pressure  $C_p$  decreases rapidly when mass fraction of the isobutyric acid increases at different temperatures.  $C_p$  is not affected by the correlation of the concentration fluctuations at the critical composition  $x_c = 0.111$  (Hadded and Bouanz, 2007).

Densities and viscosities of binary mixtures of aniline + benzene have been measured over the entire range of composition, at atmospheric pressure, and at 298.15, 303.15, 308.15, and 313.15 K. Excess molar volumes and deviations in viscosity have been calculated from the experimental data. Negative excess molar volume and negative deviations in viscosity for aniline + benzene systems are due to the interstitial accommodation of benzene molecules into aggregates of aniline (Kharat and Nikam, 2007).

The viscosities of 18 binary mixtures with methylcyclohexane have been measured at 303.15 K over the entire range of composition (Oswal *et al*, 2005). Viscosities of binary mixtures 1,3-dioxolane or 1,4-dioxane with isomeric chlorobutanes have been measured at 298.15 K and 313.15 K and the kinematic viscosities were correlated by the McAllister equation. The corresponding viscosity deviations were calculated and they were negative over the whole composition range for all mixtures (Giner *et al*, 2006).

Ternary mixtures are a three-part mixture of some substances; the viscosity and density have been experimentally measured of ternary liquid mixtures. Iloukhani and Rostami measured densities, dynamic viscosities of the ternary mixture diethylcarbonate (1) + p-chloroacetophenone (2) + 1-hexanol (3) near 303.15K and 1 atm (Iloukhani and Rostami, 2008). The viscosity and density of other ternary mixture of water + butyl acetate + methanol and water + ethyl Propionate + methanol were measured at different temperatures by Zoran and his group (Zoran *et al*, 2000).

Densities, viscosities and ultrasonic sound speed of pure propiophenone, p-methylacetophenone, p-chloroacetophenone and those of their binary mixtures prepared using N,N-dimethylaniline as a common component were measured at 303.15K and 308.15K over the entire composition range (Gowrisankar *et al*, 2012).

The density and viscosity of binary 1-hexene + 1-octene mixtures have been simultaneously measured over the temperature range from (298 to 470) K and at pressures up to 196 MPa using a hydrostatic weighing and falling-body techniques (Damir *et al*, 2014). Dynamic viscosities of four

binary mixtures have been measured at 303.15, 308.15, 313.15, 318.15 and 323.15 K and atmospheric pressure. Viscosity deviations for the binary systems were fitted to the Redlich-Kister polynomial equation. (Emila *et al*, 2010).

Abdelraziq and his group measured ultrasonic velocity and absorption as a function of temperature, concentration, and frequency (5-25 MHz) and shear viscosity as a function of concentration and temperature. The system of nitrobenzene and n-hexane has critical temperature 19.89 °C and a critical composition  $x_c$  of 51.70% by weight of nitrobenzene (Abdelraziq *et al*, 1990).

Abdelraziq and his group measured the ultrasonic velocity and absorption and shear viscosity as a function of concentration and temperature for some binary liquid solutions (Abdelraziq *et al*, 1989; Abdelraziq *et al*, 1992). The existence of shear viscosity anomaly has been experimentally observed in the binary liquid mixture methanol - cyclohexane near the critical temperature  $T_c = 45.2$  °C and the critical concentration  $x_c = 30\%$  by weight of methanol (Omar, 2014).

Ultrasonic absorption measurements were made as a function of temperature and frequency for the binary mixture of cyclohexane and aniline. The absorption coefficient for critical concentration increases as the critical temperature is approached from high-temperature region for all frequencies (Abdelraziq, 1996). The velocity for the critical mixture increases with increasing frequency. This indicates the dispersion in the



sound velocity was as expected for binary liquid mixtures (Abdelraziq, 2000).

Abdelraziq and his group measured the shear viscosity as a function of temperature for the binary mixture of nitrobenzene and n-heptane. The results above the critical temperature were analyzed by the mode coupling theory. The anomaly of viscosity was detected as a function of temperature and concentration (Abdelraziq, 1997).

Two types of viscosity were studied for different aqueous solutions; for example Kestin and his group tabulated values of dynamic and kinematic viscosity of NaCl solution in the temperature range 20-150 °C, pressure range 0.1-30 MPa and concentration range 0-5.4 molal (Kestin *et al*, 1981). Some researchers studied the dynamic viscosity of different materials such olive oil as a function of temperature, storage age, and intensity of light, pressure, molecular weight and density of liquid (Niarat *et al*, 2014).

The theoretical understanding of liquid-liquid mixture is very important. The knowledge of physicochemical properties of these mixtures are important for many chemical process industries. Petroleum and petrochemical are some examples to be mentioned. These types of mixtures are commonly used in industries where physicochemical processes are involved to handle the mixtures of hydrocarbons, alcohols, aldehydes and ketones (Rice, 1949).

### **1.3 Objectives of the Study**

The main goals of this study are

1. Applying the mode coupling theory approach to determine the noncritical part of shear viscosity  $\eta_0$ .
2. Determining critical isobaric specific heat  $c_{pc}$ , isobaric thermal expansion coefficient  $\alpha_p$ , Joule's constant  $J$  and pressure derivation of the critical temperature  $T_c'$ .
3. Determining the behavior of mass density as a function of temperature (power law).

In order to achieve the main objectives, some steps have been done:

1. Measuring the dynamic shear viscosity coefficients  $\eta$  for the binary mixture cyclohexane – phenol over the entire of concentration as a function of and over range of temperature.
2. Detecting the critical temperature and critical concentration of cyclohexane – phenol binary mixture.

#### **1.4 Hypothesis**

- At the critical point, there will be sharp changes in thermodynamic properties.
- Cyclohexane - phenol binary mixture exhibits anomaly at certain concentration (critical concentration). The power law can set up of the binary mixture at the critical concentration and above the critical temperature.

#### **1.5 Novelty of this Work**

- Measuring the dynamic shear viscosity for cyclohexane - phenol binary mixture has been conducted here for the first time.

- In this work, the power law of mass density has been established for the first time. No other people managed to set up the power law for any binary mixture. This work is the first to do for cyclohexane – phenol.

## **1.6 Thesis Layout**

The first chapter of the thesis is the introduction which presents definitions of binary liquid mixture beside previous researches which were discussing the binary liquid mixtures and their properties, objectives of the study. In chapter two the theories concerned with binary mixtures as mode coupling theories and the two – scale – factor universality are discussed. The methodology of the experiment is presented in chapter three: The characteristics of the binary mixture components, experimental apparatus, procedure, statistical analysis. The measured data will be given in chapter four, the viscosity data near the critical point will be analyzed using the mode coupling theory. The two – scale – factor universality for isobaric thermal expansion coefficient is used to fit the data near the critical point, the power law is expected for the mass density. In chapter five, the conclusion of this work and future works will be displayed.

## Chapter Two

### Theory

#### 2.1 Viscosity

Viscosity is the tendency of a fluid to resist flow and can be thought of as the internal friction of a fluid. Microscopically, viscosity is related to molecular diffusion and depends on the interactions between molecules. The opposite of the viscosity is the fluidity that measures the mobility for fluid layers (Secco *et al*, 2013). Viscosity is affected by the temperature and composition of the fluid and for compressible fluid, also by pressure (Serway *et al*, 2012).

The shear viscosity of a fluid can be expressed in two distinctive forms:

##### 1. The dynamic viscosity

The dynamic viscosity is defined as the ratio of shear stress (force over cross section area) to the rate of deformation.

$$\eta = \frac{\tau}{\frac{dy}{dx}} \quad (2.1.1)$$

Where  $\eta$  the dynamic viscosity,  $\tau$  is is shear stress between two adjacent layers in a flowing liquid ( $\frac{N}{m^2}$ ) and  $\frac{dy}{dx}$  is rate of deformation (shear rate) ( $\frac{1}{s}$ ). The dynamic viscosity units are Centipoise (cP) which is  $10^{-2}$  of Poise (Dutt *et al*, 2007).

##### 2. Kinematic viscosity

The kinematic viscosity is the ratio of viscosity  $\eta$  to mass density  $\rho$  (taken at the same temperature and pressure).

$$\mu = \frac{\eta}{\rho} \quad (2.1.2)$$

Kinematic viscosity is normally expressed in terms of Centistokes and  $\rho$  is mass density in  $\frac{\text{gm}}{\text{cm}^3}$  (Druk *et al*, 1966).

The flow characteristics of liquids are mainly dependent on viscosity and are broadly divided into two categories (Viswanath *et al*, 2007):

1. Newtonian fluids

The viscosity of these fluids remains constant and is independent of the applied shear stress (rpm).

2. Non-Newtonian fluids

The viscosity of these fluids depends on the applied shear force and time.

## 2.2 Pure-Liquid Viscosity Theories

The effect of temperature on kinematic viscosity is in the form of an Arrhenius-type relationship (Clements *et al*, 2006).

$$\mu = A e^{\frac{E_a}{RT}} \quad (2.2.1)$$

Where  $\mu$  is the kinematic viscosity in  $m^2 s^{-1}$ ,  $E_a$  the activation energy for flow,  $R$  is the universal gas constant,  $T$  is the absolute temperature and  $A = \frac{h N_A}{V}$ . Where  $N_A$ ,  $V$  and  $h$  are the Avogadro's number, the molecular volume and the Plank's constants respectively.

Dynamic viscosity  $\eta$  for pure liquid calculated from the kinematic viscosity  $\mu$  and the density  $\rho$  according to equation (2.1.2).

The viscosity of pure liquids is affected by on temperature, pressure, density, and surface tension (Dutt *et al*, 2007). When the temperature drops the particles slow down and come closer together, the forces of attraction

between them will increase and so make it harder for them to flow past each other. The dynamic viscosity of liquids increases with decreasing temperature (Binder *et al*, 2007).

### **2.3 Dynamic Viscosity of Mixtures**

The behavior of the viscosity is like pure liquids far from the critical point of a binary liquid mixture, but around the critical point, the situation becomes more complicated (Barmatz and Hahn, 2007). The Mode Coupling Theory is used to study the critical points anomaly of the shear viscosity and the coefficients.

Mode Coupling Theory is applied when the modes of one fluid perturbed by the modes of the other, these perturbations lead to coupling and exchange of energy (Little and Huang, 1995). This means the start of the interaction between the fluids layers. It starts originally by Fixman who proposed mechanisms by which the relaxation time and the kinetic coefficients - e.g. viscosity - for the order parameter - e.g. density - could diverge at a critical point (Fixman, 1962).

### **2.4 Shear Viscosity Near the Critical Point:**

The mode coupling approach of Perl and Ferrell predicts a critical anomaly of the shear viscosity coefficient according to the law (Perl and Ferrell, 1972; Abdelraziq; 2002):

$$\frac{\eta - \eta_0}{\eta} = \frac{\Delta\eta}{\eta} = A \ln(\xi) + A \ln(q_D) \quad (2.4.1)$$

where  $\eta_0$  is the noncritical part of the measured shear viscosity in cP, A is a MCT universal constant predicted to have the theoretical value  $\frac{8}{15 \pi^2} \approx$

0.054,  $q_D$  is the upper cutoff wave number (Debye momentum cutoff) in  $\text{\AA}^{-1}$  and  $\xi$  is the correlation length of the concentration fluctuations in  $\text{\AA}$ .

The shear viscosity  $\eta$  is temperature dependent at the critical concentration as  $T$  approaches  $T_c$ ,  $\eta$  increases indefinitely. The resulting singularity is also of the power law type (Klein and Woermann, 1978; Abdelraziq; 2002):

$$\eta = \eta_0 \tau^{-x_\eta \nu} \quad (2.4.2)$$

Here  $\eta_0$  is the noncritical part of the dynamic shear viscosity,  $\tau$  is the reduced absolute temperature  $\tau = \frac{T-T_c}{T_c}$  and  $x_\eta$  and  $\nu$  are critical exponents,  $\nu = 0.64$ ,  $x_\eta \nu = 0.04$ .

## 2.5 Density

The behavior of a fluid in flow is very much related to two intrinsic properties of the fluid: density and viscosity. Density is a measure of the mass per unit of volume of that substance. When the temperature drops the particles slow down and come closer together, the fluid volume decreases. It is an accepted fact that Pure Liquid density decreases linearly with increasing temperature. This relationship can be expressed mathematically as

$$\rho = a + b T \quad (2.5.1)$$

Where  $\rho$  is the density,  $T$  is the temperature, "a" is the intercept and "b" is a negative slope.

## 2.6 Density Correlation Function

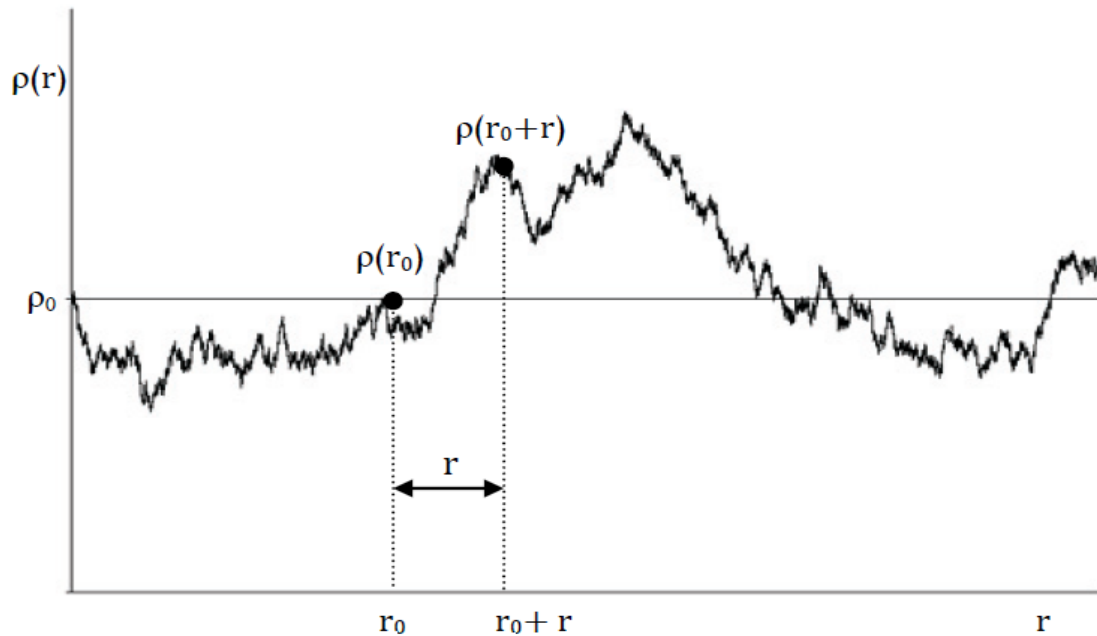
Mode coupling approach is used to clarify the critical dynamics of the binary Van der Waals mixtures. Some of the concepts in the MCT will be first defined; density fluctuations  $\rho(r)$  and density correlation function  $C(r)$ .

In a system of  $N$  particles the density distribution  $\rho(r)$  can be described as (Reichman and Charbonneau, 2005):

$$\rho(r) = \sum_j \delta(r - r_j) \quad (2.6.1)$$

Where  $r_j$  positions of particles and  $j = 1, 2, 3 \dots, N$ .

The most important observable is the density fluctuations  $\rho(r)$  in the mode coupling approach, which fluctuates around the average density  $\rho_0$  in equilibrium as shown in Figure 2.1.



**Fig. (2.1)** Space evolution instantaneous fluctuations of the density  $\rho(r)$  (Reichman and Charbonneau, 2005)



How much a correlation exists between the fluctuations in two points a distance apart can be measured by a correlation function  $C(r)$  which represents the average product of the fluctuations  $\rho(r_0)$  and  $\rho(r_0 + r)$  in two points a distance  $r$  (the correlation length) apart  $\langle \rho(r_0)\rho(r_0 + r) \rangle$  as shown in Figure 2.1, divided by the average square of the fluctuations  $\langle |\rho(r)|^2 \rangle$  (Debye, 1959):

$$C(r) = \frac{\langle \rho(r_0) \rho(r_0+r) \rangle}{\langle |\rho(r)|^2 \rangle} \quad (2.6.2)$$

$C(r)$  gives the probability to find a particle in the volume element  $dr$  located at  $r_0 + r$ , if there is another particle at  $r_0$ .

Density correlation function analysis with ordered or disordered structures, calculation of average coordination numbers can be related to structure factor measured in neutron and X-ray scattering experiments.

## 2.7 Power Law

The singular behaviour of the binary mixture around the critical point is characterized by a set of critical exponents. These exponents describe the non-analyticity of various thermodynamic functions, Thermophysical quantities typically exhibit power-law behavior in the asymptotic region that are very close to a critical point, depending on the thermodynamic path by which it is approached. The values of critical exponents depending only on very general properties, such as dimensionality and not on specific details of the interactions (Cheung, 2011).

The dynamic shear viscosity  $\eta$ , correlation length  $\xi$ , isobaric specific heat  $c_p$ , isobaric thermal expansion coefficient  $\alpha_p$ , mass density  $\rho$ ,

susceptibility and refractive index near the critical point can be written as a power law.

Some thermodynamic properties diverge as the critical temperature  $T_c$  is getting close to the divergence power-law in  $|T - T_c|$ , whereas other thermodynamic properties show a non-divergent power-law. The exponents that go with these power laws are called critical exponents (Qasim and Darwish, 2013).

Regardless of critical point, transport properties coefficients related to heat and mass transport in binary mixtures are non-singular and slowly varying functions of the temperature caused by the increase of the correlation length  $\xi$ . This regular behavior is extrapolated into the critical region, one arrives at a separation of transport coefficients into the critical contributions and background contributions (Strathmann, 2002).

The correlation length  $r$  have the symbol  $\xi$  in the MCT, it measures the range of density fluctuations in real space. The correlation length  $\xi$  is a measure of the distances over which the density–density correlations in the system extend. However, as  $\rho = \rho_c$  and  $T$  approaches  $T_c$ ,  $\xi$  increases indefinitely. The resulting singularity is also of the power law type (Pathria and Beale, 2011):

$$\xi = \xi_0 \tau^{-\nu} \quad (2.6.3)$$

This is related to the reduced temperature  $\tau$  near the critical temperature and critical concentration and  $\xi_0$  is the critical amplitude of correlation length.

The different critical exponents for the binary liquid mixture are presented in Table (2.1).

**Table (2.1) Experimental data on critical exponents for binary fluid mixtures (Iwanowski and Sorau, 2007)**

Exponent	Value
$\alpha, \alpha'$	0.05-0.15
$\beta$	0.30-0.34
$\gamma$	1.2-1.4
$\delta$	4.0-5.0
$\nu$	0.64

Here the quantities  $\alpha$ ,  $\alpha'$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\nu$  are critical exponents, which are predicted to be invariant from binary system to binary system.

The static scaling hypothesis provides relations between the critical exponents of different parameters by scaling laws

Rushbrooke scaling:

$$2 - \alpha = \beta(\delta + 1) \quad (2.8.1)$$

Josephson scaling:

$$2 - \alpha = \nu \quad (2.8.2)$$

Where  $\alpha$  is the constant-volume specific-heat exponent and  $\beta$  describes the shape of the coexistence curve.

The dynamic scaling hypothesis, which describes the phenomenon of critical slowing down, was firstly introduced by Ferrell in 1967.

## **2.8 Two – Scale – Factor Universality**

The two – scale – factor universality has played a central role in study of phase transition. It explains the critical phenomena of binary liquid

mixtures by prediction (Hohenberg *et al*, 1976; Abdelraziq, 2003). This quantity is defined as:

$$R_{\xi} = \xi_0 \left( \frac{\alpha \rho_c c_{pc}}{K_B} \right)^{\frac{1}{d}} = \xi_0 \left( \frac{\alpha T_c \alpha_{pb}}{K_B T_c'} \right)^{\frac{1}{d}} = 0.270 \quad (2.8.1)$$

Where  $\xi_0$  is the universal quantity  $\alpha$  is the critical exponent and it is equal 0.11,  $\rho_c$  the mass density is at the critical temperature,  $c_{pc}$  the critical isobaric specific heat,  $K_B$  is the Boltzmann's constant it is equal  $1.38 \times 10^{-23} \frac{\text{Joule}}{\text{K}}$ ,  $T_c$  is the critical temperature,  $\alpha_{pb}$  is the background isobaric thermal expansion,  $T_c' = \frac{dT_c}{dP}$  and is the pressure derivation of the critical temperature along the critical line.

The isobaric specific heat is given by:

$$c_p = c_{pc} \tau^{-\alpha} + c_{pb} \quad (2.8.2)$$

Where  $c_{pc}$  is the critical isobaric specific heat,  $c_{pb}$  and is the background of specific heat at constant pressure,  $\tau = \frac{T-T_c}{T_c}$  is the reduced absolute temperature and  $\alpha$  is the critical exponent.

isobaric thermal expansion coefficient which can be expressed as:

$$\alpha_p = \alpha_{pc} \tau^{-\alpha} + \alpha_{pb} \quad (2.8.3)$$

Where  $\alpha_{pc}$  is the critical isobaric thermal expansion coefficient and  $\alpha_{pb}$  is the background terms in isobaric thermal expansion coefficient

## Chapter Three

### Methodology

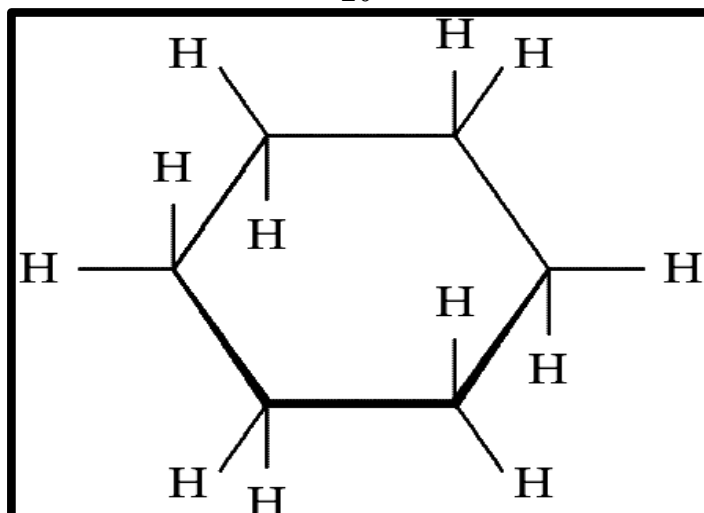
The samples of cyclohexane and phenol were used, in this work. The shear viscosities from 14.0 to 21.0 °C temperature range were measured for cyclohexane – phenol binary mixture, over the different concentrations from 0.00% to 40.00% of phenol. The concentration and temperature dependence of shear viscosity were measured. Each measured data of the viscosity of cyclohexane – phenol samples represents the average of three measurements. The experimental data were fitted and the critical temperature and concentration were obtained.

#### 3.1 The Characteristics of the Binary Mixture Components

##### 1. Cyclohexane:

Cyclohexane is a colorless organic solvent, which is fractionated from petroleum and exists as a liquid at STP with the molecular formula  $C_6H_{12}$ . Its molecule is composed of 6 carbon atoms joined in a ring, with 2 hydrogen atoms attached to each carbon atom. The ideal bond angle for a tetrahedral atom would be 109.5 degrees (Gad, 2014). High-purified cyclohexane (99.60%) was used. Cyclohexane is mainly used as a synthesis intermediate product for the manufacture of nylon. It may be presented in some consumer products (such as e.g. coatings, cleaning agents, paints, fuel).

The molecular structure of planar cyclohexane is given in Fig.(3.1).

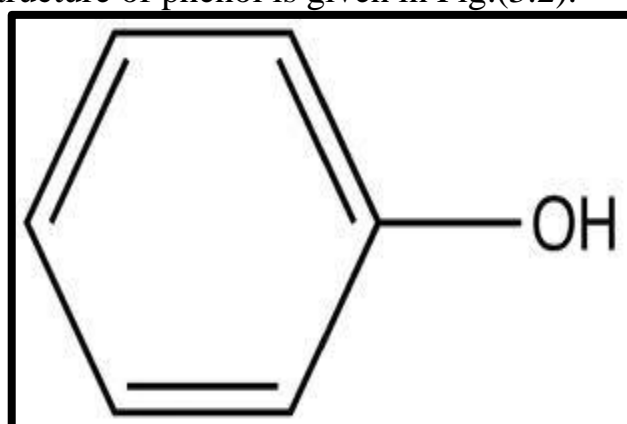


**Fig.(3.1)** The molecular structure of cyclohexane

## 2. Phenol

Phenol is an organic compound that is found naturally with the molecular formula  $C_6H_5OH$ , white crystalline solid at room temperature, also known as carbolic acid and phenic acid, It has various applications in medicine, and manufacturing of plastics, fertilizers, paints, rubber, adhesives, paper, and soap (Abdollahi, 2014). High-purified phenol (99.90%) was used. Phenol and its chemical used to building polycarbonates, epoxies, Bakelite, nylon, detergents, and numerous pharmaceutical drugs.

The molecular structure of phenol is given in Fig.(3.2).



**Fig.(3.2)** The molecular structure of phenol

The characters of cyclohexane and phenol are shown in Table (3.1):

**Table (3.1) Physical and chemical properties of cyclohexane and phenol**

Property	Cyclohexane (Colette <i>et al</i> , 2003)	Phenol (Frumkin and Gerberding, 2008)
Molecular weight	84.2 (gm/mole)	94.111 (gm/mole)
Physical state (20°C)	Liquid	Crystalline solid
Color	Colorless	Colorless
Density (20 °C )	0.7785 gm/cm <sup>3</sup>	1.0710 gm/cm <sup>3</sup>
Melting point	6.47 (°C )	40.9 (°C )
Boiling point	80.7 (°C )	181.8 (°C )
Viscosity (20 °C)	1.0 (cP)	11.3 (cP)
Water solubility (at 25°C)	55 mg/L	8.28 × 10 <sup>4</sup> mg/L
Vapor pressure (at 25°C)	97 mmHg	0.35 mmHg

### 3.2 Experimental Apparatus

#### ▪ Density Apparatus

The density of the binary liquid mixture cyclohexane – phenol was measured, The instruments that were used to measure it are:

- Pycnometer (Density bottle) of 10ml with accuracy  $\pm 0.0005\%$ , Pycnometer is used to keep a constant volume of the measured sample and it is usually made of glass with a close-fitting ground glass stopper with a capillary tube through it. Air bubbles may escape from the apparatus, Pycnometer is shown in Fig.(3.3).



**Fig. (3.3)** Pycnometer of 10ml for density measurement

- The analytical balance HR-200 with accuracy of  $\pm 0.00005\%$  was used to measure the mass of cyclohexane and phenol. It is shown in Fig.(3.4).



**Fig. (3.4)** Analytical balance HR-200 to measure the mass



- **Temperature Apparatus**

The temperature was measured using Appa 51 Digital Thermometer (with K-probes optional). The accuracy of this apparatus is  $\pm(0.3\% + 1^\circ\text{C})$  and the range of the temperature it measures from  $-50^\circ\text{C}$  to  $1300^\circ\text{C}$  resolution  $0.1^\circ\text{C}$  to  $1.0^\circ\text{C}$ . It is shown in Fig. (3.5).



**Fig. (3.5)** Appa 51 Digital Thermometer

Julabo F25-MV Refrigerated and Heating Circulator is used to measure and control the temperature of the samples to a specific temperature Fig.(3.6).

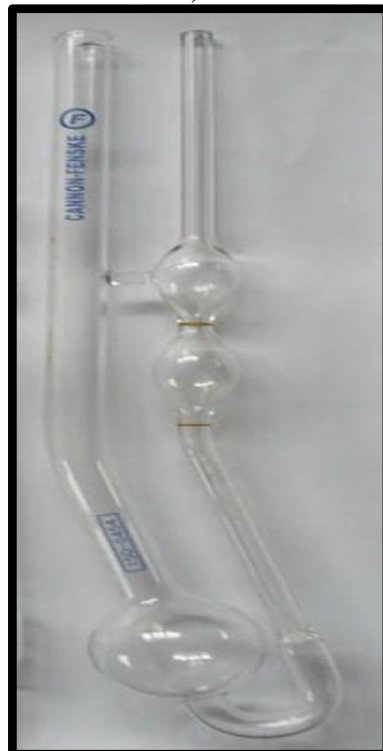


**Fig. (3.6)** Julabo F25-MV Refrigerated and Heating Circulator

### ▪ Viscosity Apparatus

The instruments that were used to measure the viscosity of cyclohexane and phenol binary mixture for different concentrations at various temperatures are glass capillary viscometers and Stopwatch:

- The standard viscometer is the instrument with a capillary diameter of 0.45 mm and a capillary length of 400 mm as shown in Fig.(3.7). The determination of the viscosity of water  $\eta = 1.0019 \text{ cP} \pm 0.0003 \text{ cP}$  at (20 °C). The capillaries of viscometers used for industrial applications are usually shorter (70 - 250 mm).



**Fig. (3.7)** Glass capillary viscometer

- The instrument that is used to measure the time ACCUSPLIT Pro Survivor - A601X Stopwatch the range of the time it measures from 0 to 24 Hrs and timing interval 1/100 Sec.

- **Joule`s Constant Apparatus**
- Calorimeter consists of an apparatus that is used for measuring the amount of heat absorbed during a physical transformation or chemical reaction. Glass calorimeter has been built to avoid the effect of phenol on metals. This glass calorimeter consists of a coil made of iron wire shield by a glass tube. The sample was put inside pyrex beaker. As shown in Fig. (3.8).



**Fig.(3.8)** Calorimeter components

Calorimeter set up is used to measure the heat capacity. The set has calorimeter, digital voltmeter, digital ammeter, and power supply as shown in Fig.(3.9).



**Fig.(3.9)** Calorimeter set up

### 3.3 Procedure

#### 1. Density Measurements.

The density for cyclohexane – phenol has been measured at different temperatures using the pycnometer. The mass of empty pycnometer is measured then when the pycnometer is filled with the mixture the mass was measured. The two masses are subtracted. The result is the mass of the binary mixture. The density is calculated by dividing the mass of the cyclohexane – phenol by the volume of the pycnometer. Binary mixture samples with different concentration should be prepared at the same temperature while the density is measured, because the density is affected by the temperature. High-purified Ethyl alcohol (99.9%) is used to clean the pycnometer.

The density for both cyclohexane and phenol separately is measured at room temperature which is for cyclohexane  $0.7647 \frac{\text{gm}}{\text{cm}^3}$  and phenol  $1.0476 \frac{\text{gm}}{\text{cm}^3}$ .

## **2. Binary Liquid Mixture (Cyclohexane – Phenol) Samples Preparation.**

Concentrations are prepared from 0.00% to 40.00% by weight of phenol. The concentration of phenol in a given sample of cyclohexane and phenol in a given volume  $V$  can be calculated from equation (3.3.1):

$$X_{\text{phenol}} = \frac{\rho_{\text{phenol}} \times V_{\text{phenol}}}{\rho_{\text{phenol}} \times V_{\text{phenol}} + \rho_{\text{cyclohexane}} \times V_{\text{cyclohexane}}} \quad (3.3.1)$$

Where  $\rho_{\text{phenol}}$  the density of phenol is,  $V_{\text{phenol}}$  is the volume of phenol,  $\rho_{\text{cyclohexane}}$  is the density of cyclohexane, and  $V_{\text{cyclohexane}}$  is the volume of cyclohexane.

## **3. Viscosity Measurements.**

The viscometer consists of a U-shaped glass tube is held vertically in a controlled temperature path. In one arm of the U-shaped glass is a vertical section of precise narrow bore. Above this narrow bore, there is a bulb. There is another bulb located on the second arm with lower level. Liquid is risen up to the upper bulb by suction, and then the liquid is allowed to flow down through the capillary into the lower bulb. The time is taken for the level of the liquid to pass between these bulbs is proportional to the viscosity and has been measured using the stopwatch. High-purified Ethyl alcohol (99.90%) is used to clean the viscometer

The viscosity of each sample was measured at temperature range from 14.0°C to 21.0°C, The viscosity of the binary mixture at different temperatures is calculated by using:

$$\eta_{binary} = \frac{\eta_{water} \rho_{binary} t_{binary}}{t_{water} \rho_{water}} \quad (3.3.2)$$

Where  $\rho_{binary}$  is density of binary mixture,  $\rho_{water}$  is density of water,  $t_{binary}$  is flow time of binary,  $t_{water}$  is flow time of water, and  $\eta_{water}$  is viscosity of water at certain temperatures.

Viscosity of water at temperature from 0.0°C to 20.0°C is given by:

$$\log_{10} \eta = \frac{1301}{998.33 + 8.1855(T-20) + 0.00585(T-20)^2} - 1.30233 \quad (3.3.3)$$

Where T is temperature (°C).

Viscosity of water at temperature above 20.0°C is given by:

$$\log_{10} \frac{\eta}{\eta_{20}} = \frac{1.3272(20-T) - 0.001053(T-20)^2}{T+105} \quad (3.3.4)$$

Where T is temperature (°C) and  $\eta_{20}$  is viscosity of water at 20.0°C

(David, 1985).

#### 4. Heat Capacity Measurement.

The critical mixture of cyclohexane – phenol is weighed before putting in the calorimeter. The calorimeter is connected with power supply, digital ammeter, digital voltmeter. The reading of the digital ammeter equals to  $I = 0.94$  Ampere and the digital voltmeter  $V = 10.22$  Volt at different

temperatures. The timer reads the time needed to reach to the specified temperature.

The following equation is used to find the work done on the critical binary mixture

$$\begin{aligned} \text{Work} &= \text{Volt} \times \text{current} \times \text{time} \\ W &= I \times V \times t \end{aligned} \quad (3.3.5)$$

Eq.(3.3.5) is used to calculate Joule`s constant of cyclohexane – phenol binary liquid mixture

$$J = \frac{H}{W} \quad (3.3.5)$$

Where W is the work, I is the current, V is the volt, t is the time, J is joule`s constant and H is the quantity of heat.

The specific heat  $c_b$  of the binary mixture at different T is calculated by using:

$$H = (m_o c_o + m_w c_w + m_u c_u + m_b c_b) \Delta T \quad (3.3.7)$$

Where: H = the quantity of heat,  $m_o$  = mass of calorimeter beaker,  $m_w$  = mass of wire,  $m_u$  = mass U tube,  $m_b$  = mass of the binary mixture,  $c_o$  = specific heat of calorimeter beaker,  $c_w$  = specific heat of wire,  $c_u$  = specific heat of U tube,  $c_b$  = specific heat of the binary mixture at critical concentration and  $\Delta T$  is the difference in temperatures.

### 3.4 Statistical Analysis

The measured data are tabulated and fitted statistically using statistical program (Microsoft Office Excel). The coefficient  $R^2$  is calculated for each curve; it represents the percent of the data that is the closest to the line of best fit.

## Chapter Four

### Results and Discussion

#### 4.1 The Critical Temperature and Critical Concentration

This section has been done in collaboration with other group members to investigate the  $x_c$  and  $T_c$ . The main objective of this work starts with section 4.2.

The dynamic viscosity values of binary liquid mixture cyclohexane – phenol samples of different concentrations (0.00%-40.00%) by weight of phenol are measured at temperature range (14.0-21.0°C) and given in Table (4.1) and Table (4.2).

**Table (4.1) The dynamic viscosity values of cyclohexane – phenol samples of different concentrations (0.00%-16.00%) by weight of phenol at temperature range (14.0-21.0°C)**

T (°C)	$\eta$ (cP) 0.00%	$\eta$ (cP) 2.00%	$\eta$ (cP) 2.70%	$\eta$ (cP) 3.40%	$\eta$ (cP) 6.70%	$\eta$ (cP) 9.90%	$\eta$ (cP) 13.20%	$\eta$ (cP) 16.00%
14.0	1.0243	0.9615	0.9851	1.0107	1.0366	1.0671	1.1177	1.3232
15.0	1.0150	0.9395	0.9774	0.9924	1.0061	1.0575	1.1166	1.2987
16.0	0.9948	0.9196	0.9566	0.9687	0.9928	1.0384	1.1007	1.2822
17.0	0.9819	0.9040	0.9672	0.9646	0.9891	1.0289	1.0815	1.2677
17.5	0.9757	0.8986	0.9416	0.9556	0.9921	1.0284	1.0800	1.2611
18.0	0.9668	0.8877	0.9232	0.9455	0.9789	1.0160	1.0632	1.2435
18.5	0.9613	0.8796	0.9109	0.9386	0.9657	1.0129	1.0552	1.2282
19.0	0.9532	0.8709	0.9047	0.9285	0.9520	1.0042	1.0425	1.2073
19.5	0.9436	0.8633	0.8936	0.9144	0.9442	0.9828	1.0250	1.1899
20.0	0.9359	0.8518	0.8877	0.9133	0.9294	0.9794	1.0209	1.1789
20.5	0.9246	0.8445	0.8784	0.9001	0.9163	0.9665	1.0076	1.1743
21.0	0.9236	0.8390	0.8768	0.8997	0.9172	0.9670	1.0059	1.1624



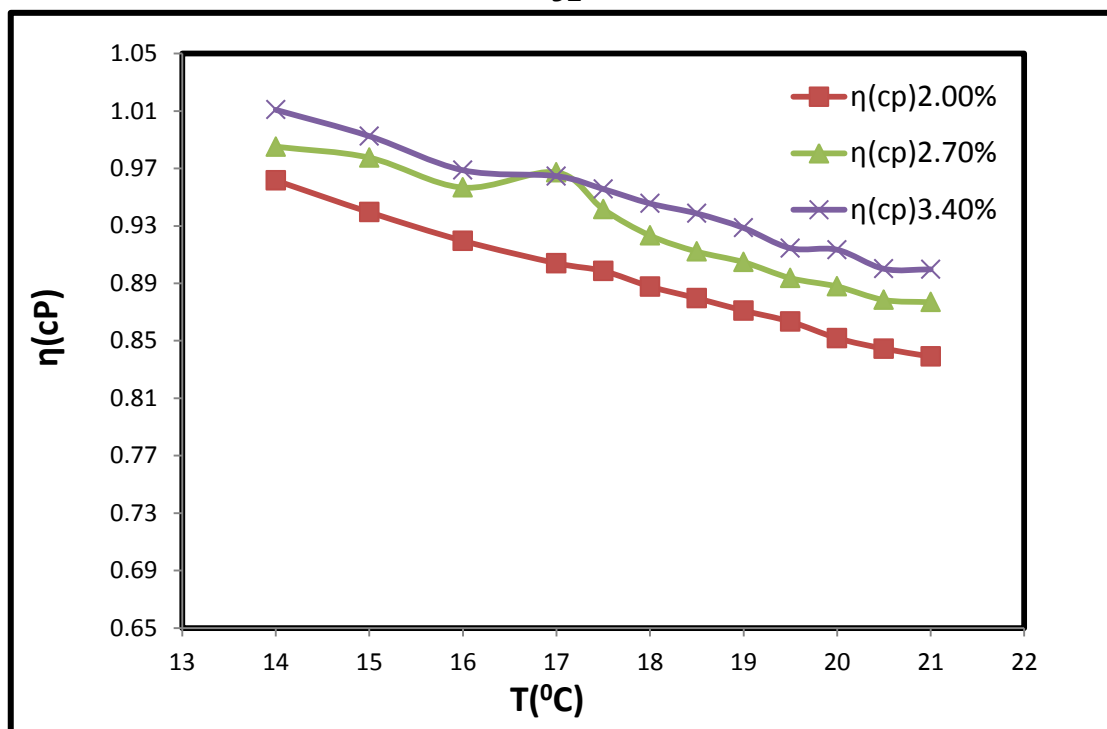
**Table (4.2) The dynamic viscosity values of cyclohexane – phenol samples of different concentrations (18.00%-40.00%) by weight of phenol at temperature range (14.0-21.0°C)**

T (°C)	$\eta$ (cP) 18.00%	$\eta$ (cP) 19.50%	$\eta$ (cP) 22.50%	$\eta$ (cP) 25.50%	$\eta$ (cP) 31.00%	$\eta$ (cP) 34.00%	$\eta$ (cP) 37.00%	$\eta$ (cP) 40.00%
14.0	1.3111	1.3707	1.4298	1.5621	1.7645	1.8601	2.1254	2.1748
15.0	1.2982	1.3372	1.3970	1.5410	1.7293	1.8188	2.0658	2.1210
16.0	1.2694	1.2928	1.3539	1.4885	1.6838	1.7887	2.0235	2.0262
17.0	1.2507	1.2364	1.3236	1.4363	1.6597	1.7639	1.9910	1.9862
17.5	1.2427	1.2346	1.3114	1.4304	1.6456	1.7443	1.9602	1.9686
18.0	1.2013	1.2224	1.2880	1.3955	1.6251	1.7077	1.9512	1.9289
18.5	1.1920	1.2219	1.2777	1.3847	1.5976	1.6772	1.8965	1.9094
19.0	1.1836	1.1936	1.2623	1.3688	1.5751	1.6499	1.8753	1.8730
19.5	1.1673	1.1670	1.2343	1.3400	1.5357	1.6051	1.8546	1.8365
20.0	1.1413	1.1568	1.2216	1.3331	1.5289	1.5895	1.8241	1.8304
20.5	1.1245	1.1444	1.2092	1.3069	1.5017	1.5693	1.7958	1.7866
21.0	1.1213	1.1330	1.1953	1.2881	1.4973	1.5370	1.7607	1.7832

Table (4.1) and Table (4.2) show that at each concentration, the viscosity decreases as the temperature increases. The heat is applied to liquids. The molecules can then slide over each other more easily making the liquid to become less viscous.

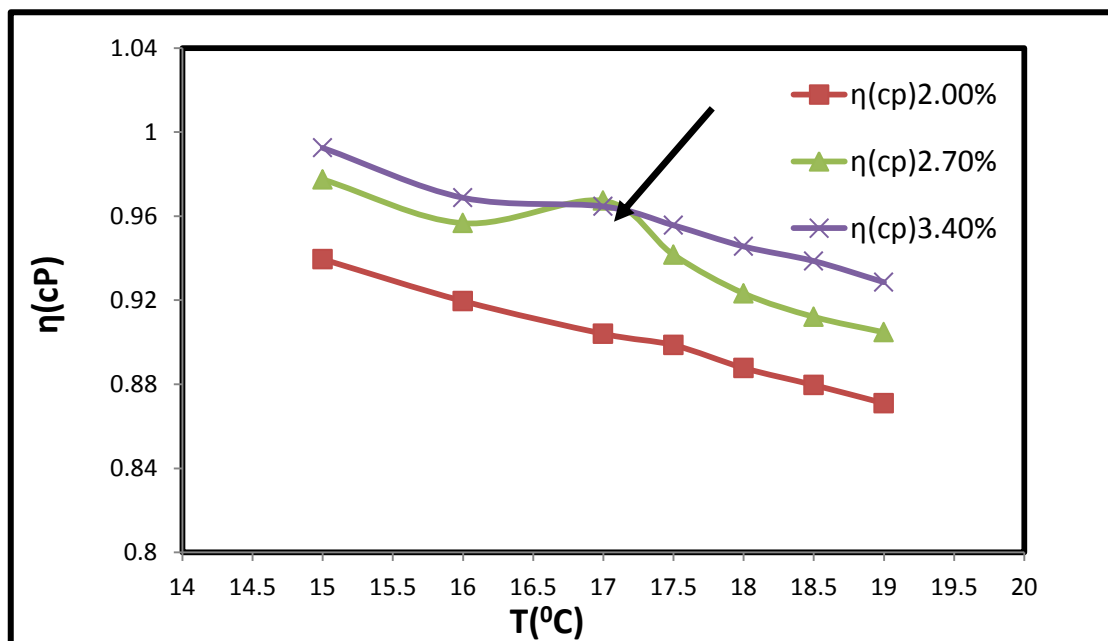
The viscosity increases as the concentration by weight of phenol increases, because phenol substance is more viscous than cyclohexane at the same temperature.

The dynamic viscosity of cyclohexane – phenol of different concentrations (2.00%-3.40%) by weight of phenol as a function of temperature are plotted in Fig.(4.1).



**Fig.(4.1)** The dynamic viscosity of cyclohexane – phenol as a function of temperature at concentrations (2.00%-3.40%) by weight of phenol

The anomaly can be noticed by plotting (2.00%-3.40%) by weight of phenol as shown in Fig.(4.2).

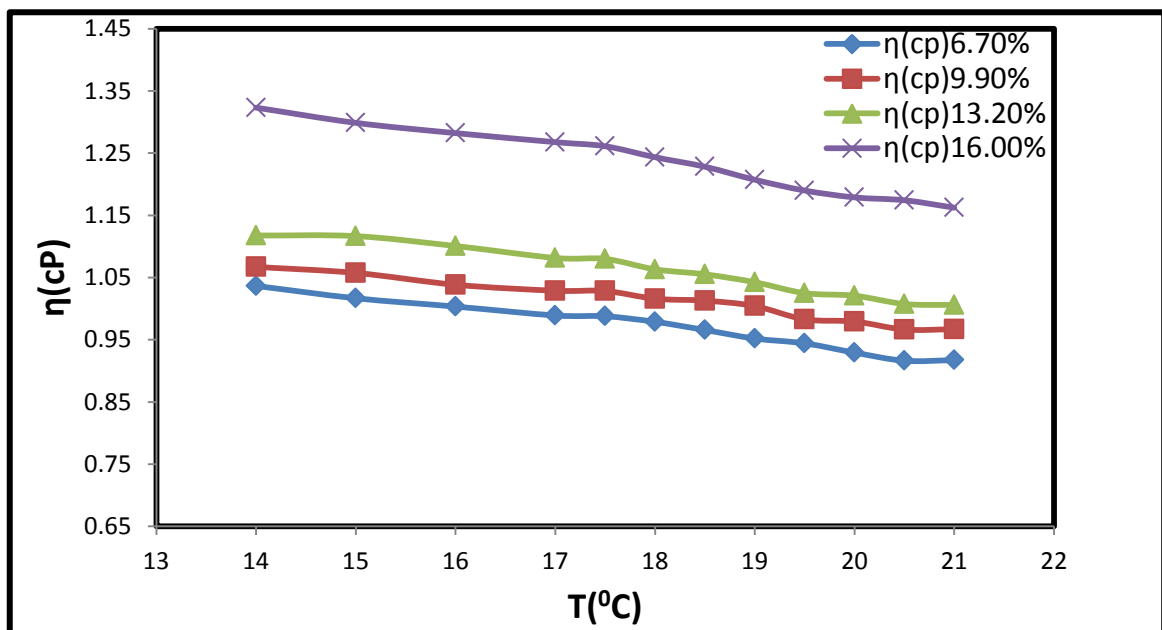


**Fig.(4.2)** The dynamic viscosity of cyclohexane – phenol as a function of temperature at concentrations 2.00% , 2.70% and 3.40% by weight of phenol

The experimental results of the dynamic viscosity of cyclohexane – phenol mixture show an anomaly at  $x_c$  and  $T_c$  in Fig. (4.2). The critical concentration  $x_c$  is 2.70% by weight of phenol and the critical temperature is determined at the highest value of the dynamic viscosity. The highest value of the dynamic viscosity is 0.9672 cP at concentration and temperature  $T_c = 17.0^\circ\text{C}$ . This point is considered to be a critical point where the two liquids become one phase.

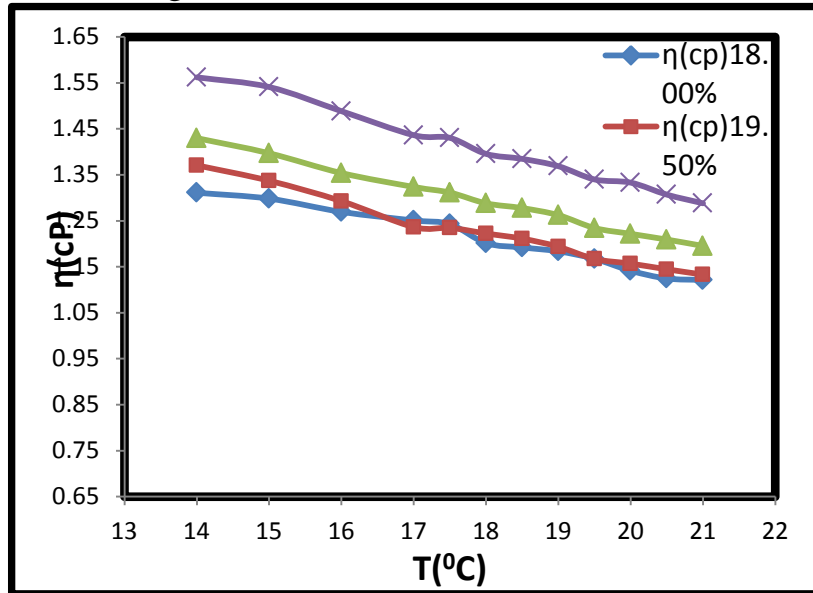
At the critical point phase boundaries vanish, cyclohexane and phenol cannot be distinguished between each other, it is the point at which an infinitesimal change in temperature will lead to separation of the mixture into two distinct liquid phases. The two clearly distinguishable liquids, cyclohexane on top of the phenol.

The experimental results of the dynamic viscosity of different concentrations (6.70%-16.00%) by weight of phenol as a function of temperature are plotted in Fig. (4.3).



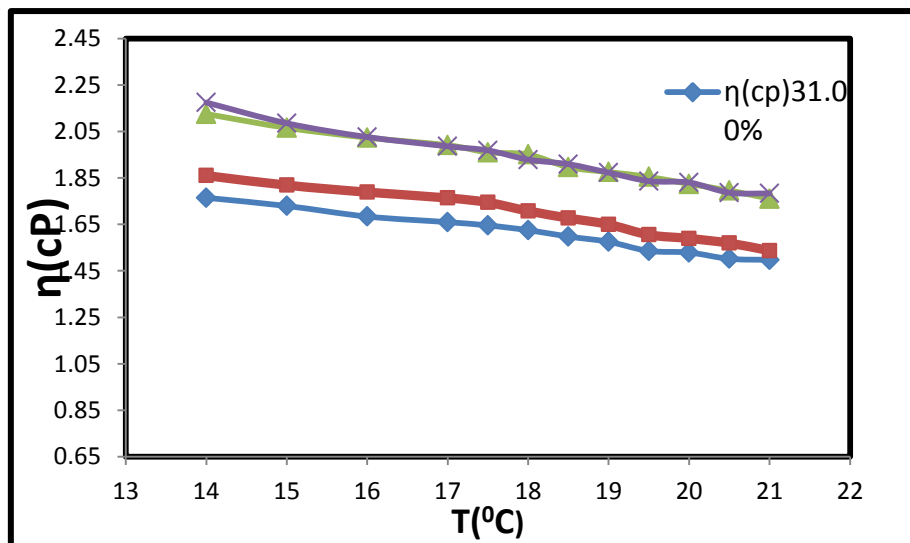
**Fig.(4.3)** The dynamic viscosity of cyclohexane – phenol as a function of temperature at concentrations (6.70%-16.00%) by weight of phenol

The experimental results of the dynamic viscosity of cyclohexane – phenol mixture showed in Fig. (4.4).



**Fig.(4.4)** The dynamic viscosity of cyclohexane – phenol as a function of temperature at concentrations (18.00%-25.50%) by weight of phenol

The dynamic viscosities of cyclohexane – phenol mixture different concentrations (31.00%-40.00%) by weight phenol as a function of temperature are plotted in Fig. (4.5).



**Fig.(4.5)** The dynamic viscosity of cyclohexane – phenol as a function of temperature at concentrations (31.00%-40.00%) by weight of phenol

The experimental results of the dynamic viscosity of cyclohexane – phenol mixture did not show an anomaly in Figs.(4.3) – (4.5). Van der Waals predicted that a phase separation could occur in a binary mixture at temperatures above the critical temperature of a binary mixture.

Dynamic viscosity of cyclohexane – phenol mixture decreases as the temperature rises. The viscosity increases with the increase of the concentration of phenol. Cyclohexane and phenol are clearly two separated liquids, where the cyclohexane is above the phenol in all other concentrations, except at the critical concentration, they become one phase and undistinguishable.

#### **4.2 The Noncritical Part of Dynamic Shear Viscosity $\eta_o$**

The dynamic Shear viscosity is temperature dependent at the critical concentration and above the critical temperature. The data of dynamic shear viscosity are fitted using the power law

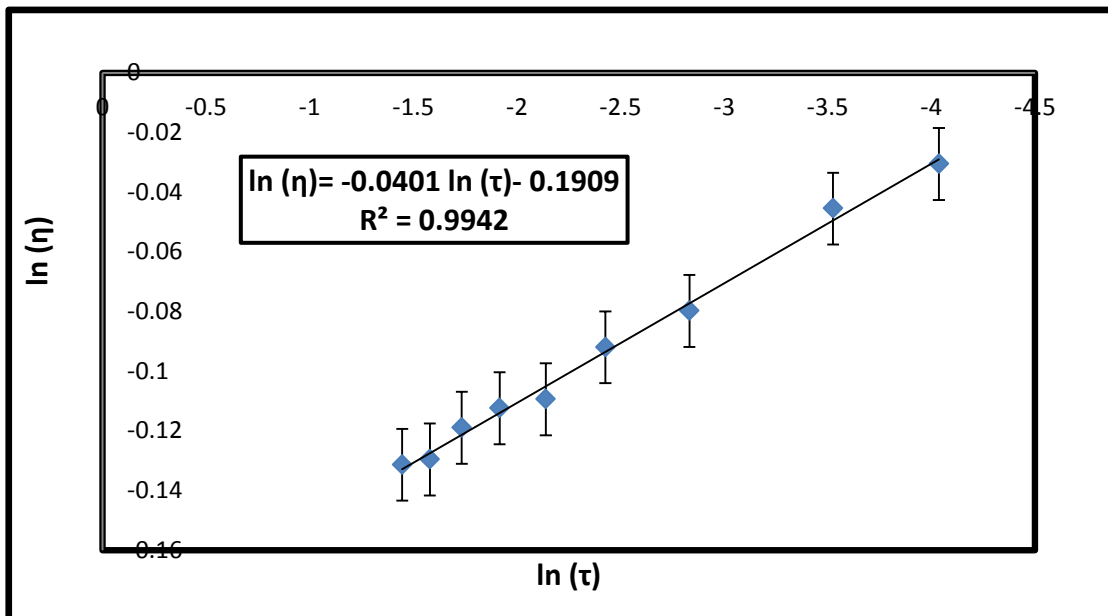
$$\eta = \eta_0 \tau^{-x_{\eta} \nu} \quad (4.2.1)$$

The data of dynamic shear viscosity coefficients  $\eta$  at the critical concentration  $x_c = 2.70\%$ , above the critical temperature  $0.1 \leq T - T_c \leq 4^\circ\text{C}$  are given in Table (4.3)

**Table (4.3)** The dynamic shear viscosity values of cyclohexane – phenol above the critical temperature  $T_c = 17.0\text{ }^\circ\text{C}$  for the critical mixture cyclohexane – phenol

$T(^\circ\text{C})$	$\eta(\text{cP})$	$T - T_c$	$\tau = \frac{T - T_c}{T_c}$	$\ln(\tau)$	$\ln(\eta)$
17.1	0.9593	0.1	0.005882	-5.1358	-5.1358
17.3	0.9539	0.3	0.017647	-4.0371	-4.0371
17.5	0.9416	0.5	0.029412	-3.5263	-3.5263
18.0	0.9232	1.0	0.058824	-2.8332	-2.8332
18.5	0.9120	1.5	0.088235	-2.4277	-2.4277
19.0	0.9047	2.0	0.117647	-2.1400	-2.1400
19.5	0.8936	2.5	0.147059	-1.9169	-1.9169
20.0	0.8877	3.0	0.176471	-1.7346	-1.7346
20.5	0.8784	3.5	0.205882	-1.5804	-1.5804
21.0	0.8768	4.0	0.235294	-1.4469	-1.4469

$\ln(\eta)$  is plotted against  $\ln(\tau)$  to find the value of the critical exponent  $x_\eta v$  as shown in Fig (4.6).



**Fig. (4.6)** Plot of  $\ln(\eta)$  versus  $\ln(\tau)$  above the critical temperature for the critical mixture cyclohexane – phenol

Fig (4.6) shows that the values of the shear viscosity fit the power law

$$\eta = \eta_o \tau^{-x_\eta \nu}$$

It represent a linear equation as follows

$$\ln(\eta) = \ln(\eta_o) - x_\eta \nu \ln(\tau)$$

The critical exponent for the critical mixture cyclohexane and phenol is the slope of Fig.(4.6) which equals to 0.0401 it is in good agreement with the critical exponent  $x_\eta \nu$  of Abdelraziq value of which equal 0.04 (Klein and Woermann; 1978, Abdelraziq; 2002).

The intercept equals  $\ln(\eta_o) = -0.1909$  , from which we can calculate the noncritical part of the shear viscosity  $\eta_o = 0.8262\text{cP}$ .

Viscosity was taken at the temperatures between 17.1°C to 21.0°C because power law is occurred at the temperature that is close to the critical temperature.

### 4.3 Thermal Expansion Coefficient

The isobaric thermal expansion coefficient and background thermal expansion for cyclohexane – phenol critical mixture is calculated by using the definition

$$\alpha_p = \alpha_{pc} \tau^{-\alpha} + \alpha_{pb} \quad (4.3.1)$$

Where:

$$\alpha_p = \rho \left( \frac{d\rho^{-1}}{dT} \right) \quad (4.3.2)$$

The thermal expansion coefficient  $\alpha_p$  can be determined by using equation (4.3.2) where  $\left(\frac{d\rho^{-1}}{dT}\right)$  is estimated from the fit of  $\rho^{-1}$  at various temperatures  $T$  ( $^{\circ}\text{C}$ ).

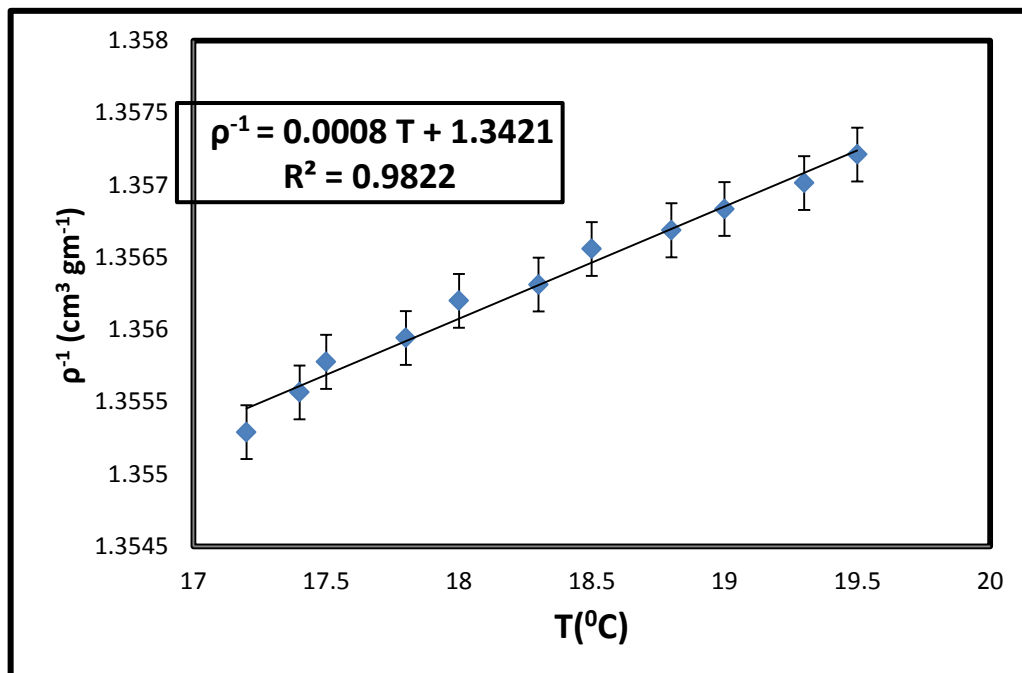
The data of the mass density  $\rho$  and its inverse  $\rho^{-1}$  are presented in Table (4.4) at different temperatures and above the critical point.

**Table (4.4) The mass density and its reciprocal values at different temperatures above ( $T_c, x_c$ )**

$T$ ( $^{\circ}\text{C}$ )	Mass density ( $\rho$ ) ( $\text{gm}/\text{cm}^3$ )	$\rho^{-1}$ ( $\text{cm}^3/\text{gm}$ )
17.2	0.7378	1.3552
17.4	0.7377	1.3555
17.5	0.7375	1.3557
17.8	0.7374	1.3559
18.0	0.7373	1.3561
18.3	0.7372	1.3563
18.5	0.7371	1.3565
18.8	0.7370	1.3566
19.0	0.7370	1.3568
19.3	0.7369	1.3570
19.5	0.7368	1.3572

The data of the reciprocal of the density are plotted as a function of temperature as shown in Fig.(4.7).





**Fig. (4.7)** The reciprocal of density for the critical mixture cyclohexane– phenol as function of temperature above ( $T_c, x_c$ )

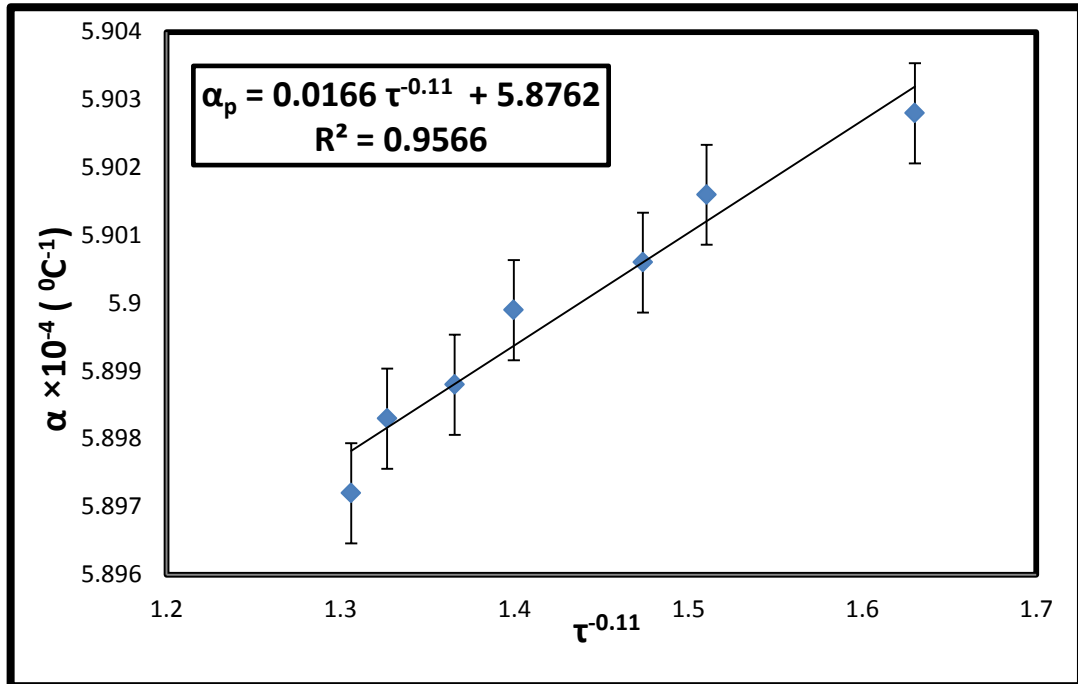
The slope of Fig. (4.7) is  $\left(\frac{d\rho^{-1}}{dT}\right) = 8 \times 10^{-4} \text{ (cm}^3/\text{gm} \cdot \text{°C)}$

The values of  $\alpha_p$  are calculated by multiplying the density at each temperature with the value of  $\left(\frac{d\rho^{-1}}{dT}\right)$ .

**Table (4.5) The isobaric thermal expansion coefficient at different temperatures for the critical mixture cyclohexane – phenol**

T(°C)	$\alpha_p \times 10^{-4} \text{ (°C}^{-1}\text{)}$	$\tau$	$\tau^{-0.11}$
17.2	5.9028	0.011765	1.630182
17.4	5.9016	0.023529	1.510507
17.5	5.9006	0.029412	1.473882
17.8	5.8999	0.047059	1.399618
18.0	5.8988	0.058824	1.365681
18.3	5.8983	0.076471	1.326831
18.5	5.8972	0.088235	1.306109

The critical and background thermal expansion coefficients can be evaluated by plotting the isobaric thermal expansion coefficients  $\alpha_p$  versus  $\tau^{-\alpha}$  as shown in Fig.(4.8).



**Fig. (4.8)** The thermal expansion coefficient for the critical mixture cyclohexane – phenol as function of  $\tau^{-0.11}$

The slope of Figure (4.8) represents the critical isobaric thermal expansion coefficient  $\alpha_{pc} = 1.66 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  according to  $\alpha_p = \alpha_{pc} \tau^{-\alpha} + \alpha_{pb}$ . The intercept of the line represents the background isobaric thermal expansion coefficient  $\alpha_{pb} = 5.87 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ .

#### 4.4 Calculation of the Pressure Derivation of the Critical Temperature

Two – scale – factor universality can be used to find the Pressure Derivation of the Critical Temperature  $T_c'$  of the cyclohexane – phenol binary liquid mixture (Hohenberg *et al*, 1976; Abdelraziq, 2002):

$$R_{\xi} = \xi_o \left( \frac{\alpha T_c \alpha_{pb}}{K_B T_c'} \right)^{\frac{1}{d}} = 0.270 \quad (4.4.1)$$

Where is the universal quantity  $\alpha$  is the critical exponent and it is equal to 0.11,  $d = 3$  is the dimension of the space,  $K_B$  is the Boltzmann's constant it is equal  $1.38 \times 10^{-23} \frac{\text{Joule}}{\text{K}}$ , the critical temperature  $T_c = 17^{\circ}\text{C}$  and the background isobaric thermal expansion  $\alpha_{pb} = 5.87 \times 10^{-4} \text{ }^{\circ}\text{C}^{-1}$ .

The pressure derivation of the critical temperature along the critical line of cyclohexane – phenol binary  $T_c' = \frac{dT_c}{dP}$  is calculated and it is equals  $1.22 \times 10^{-4} \frac{\text{K}}{\text{Pa}}$ .

#### 4.5 Calculation of the Critical Isobaric Specific Heat

Two – scale – factor universality can be used to find the critical isobaric specific heat  $c_{pc}$  of the cyclohexane – phenol binary liquid mixture (Hohenberg *et al*, 1976; Abdelraziq, 2002):

$$R_{\xi} = \xi_o \left( \frac{\alpha \rho_c c_{pc}}{K_B} \right)^{\frac{1}{d}} = 0.270 \quad (4.5.1)$$

Where critical exponent  $\alpha = 0.11$ ,  $d = 3$  is the dimension of the space, mass density at the critical temperature  $\rho_c = 0.7627 \frac{\text{gm}}{\text{cm}^3}$  (experimentally measured by pycnometer), critical amplitude for the correlation length  $\xi_o = 3.12 \text{ \AA}$  measured by Abdelraziq (Abdelraziq, unpublished results) and Boltzmann's constant is given by  $K_B = 1.38 \times 10^{-23} \frac{\text{Joule}}{\text{K}}$ .

The critical isobaric specific heat  $c_{pc}$  of cyclohexane – phenol binary liquid mixture is calculated and it is equals  $106.6 \frac{\text{Joule}}{\text{kg.K}}$ .

The isobaric specific heat and background specific heat of cyclohexane – phenol critical mixture are calculated by using the definition

$$c_p = c_{pc} \tau^{-\alpha} + c_{pb} \quad (4.5.2)$$

The data of isobaric specific heat are fitted by using equation (4.5.2).

The isobaric specific heat at the critical concentration  $x_c = 2.70\%$  above the critical temperature are given in Table (4.6)

**Table (4.6) The isobaric specific heat at different temperature for the mixture cyclohexane – phenol at critical concentration of phenol**

$T$ ( $^{\circ}\text{C}$ )	$T$	$\tau^{-\alpha}$	$c_p$ ( $\frac{\text{Calorie}}{\text{Kg.K}}$ )
18.5	0.0882	1.3061	139.23
19.0	0.1176	1.2654	134.89
19.5	0.1470	1.2347	131.62

The isobaric specific heat is used to determine the Joule`s constant.

#### 4.6 Calculation of the Joule`s Constant

The Joule`s constant  $J$  of cyclohexane – phenol is determined by using

$$J = \frac{H}{W} \quad (4.6.1)$$

Where:

$$W = I \times V \times t \quad (4.6.2)$$

$$H = (m_0 c_0 + m_w c_w + m_u c_u + m_b c_b) \Delta T \quad (4.6.3)$$

The quantity of isobaric specific heat  $c_p$  at different temperatures from Table (4.6),  $V = 10.22$  Volt and  $I = 0.94$  Ampere the critical mixture cyclohexane – phenol.

The work  $W$ , the quantity of heat  $H$ , the temperature readings and the time reading of Joule`s constant experiment are given in Table (4.7).

**Table (4.7) Joule`s constant experiment data temperatures for the critical mixture cyclohexane – phenol**

$T(^{\circ}\text{C})$	$\Delta T(^{\circ}\text{C})$	$\Delta t(\text{s})$	$W$ (Joule)	H (Calorie)	$J \left( \frac{\text{Calorie}}{\text{Joule}} \right)$
18.5	6.5	4399	42260.3	130407.3	3.1807
19.0	6.0	2978	28609.0	116640.2	4.2023
19.5	5.5	2252	21634.5	104337.5	4.9710

The Joule`s constant  $J$  evaluated temperatures close to the critical temperature. Joule`s constant values here are not constant because the specific heat changes with temperature change. The average value for Joule`s constant equals  $4.1180 \frac{\text{Calorie}}{\text{Joule}}$ .

The Joule`s constant  $J$  of cyclohexane – phenol is not equal Joule`s constant for water because Joule`s constant of water equals  $4.1860 \frac{\text{Calorie}}{\text{Joule}}$

when the temperature of 1g water is increased from  $14.5^{\circ}\text{C}$  to  $15.5^{\circ}\text{C}$ .

While average value for Joule`s constant of cyclohexane – phenol binary mixture equals  $4.1180 \frac{\text{Calorie}}{\text{Joule}}$  when it's temperature changed according to

the following values ( $25^{\circ}\text{C} - 18.5^{\circ}\text{C}$ ), ( $25^{\circ}\text{C} - 19.0^{\circ}\text{C}$ ) and ( $25^{\circ}\text{C} - 19.5^{\circ}\text{C}$ ).

#### **4.7 The Noncritical Part of Mass Density**

The mass density is expected to be temperature  $\tau$  dependent at the critical concentration  $x_c$  and above critical temperature which is given by the power law as viscosity, The power law of the mass density  $\rho$  is used to determine the background mass density  $\rho_0$ .

$$\rho = \rho_0 \tau^{-x_{\rho} v} \quad (4.7.1)$$

Where  $x_{\rho} v$  is critical exponents and  $v = 0.64$  (Klein and Woermann; 1978, Abdelraziq; 2002).

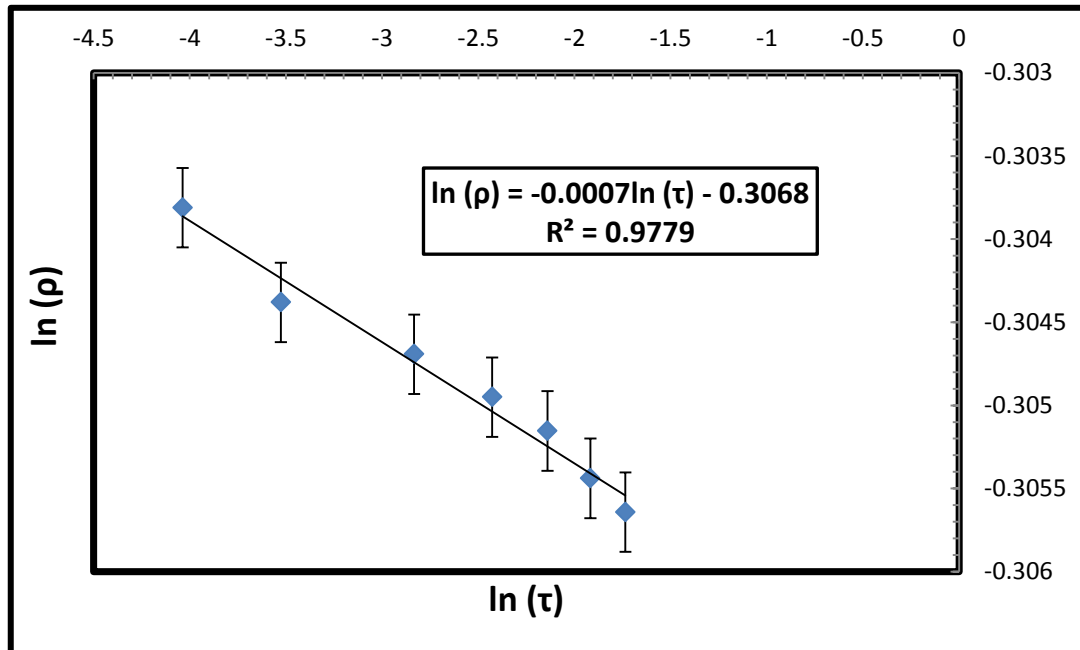
The data of density are fitted by using equation (4.7.1).

The data of density at the critical concentration  $x_c = 2.70\%$  above the critical temperature are given in Table (4.8)

**Table (4.8)** The measured density above the critical temperature  $T_c 17.0^\circ\text{C}$  for the critical mixture cyclohexane – phenol

$T(^{\circ}\text{C})$	$T - T_c$	$\tau = \frac{T - T_c}{T_c}$	$\ln(\tau)$	$\rho \text{ (gm/cm}^3\text{)}$	$\ln(\rho)$
17.3	0.4	0.023529	-3.74950	0.73800	-0.30381
17.5	0.5	0.029412	-3.52636	0.73758	-0.30437
18.0	1.0	0.058824	-2.83321	0.73735	-0.30469
18.5	1.5	0.088235	-2.42775	0.73716	-0.30495
19.0	2.0	0.117647	-2.14007	0.73701	-0.30515
19.5	2.5	0.147059	-1.91692	0.73680	-0.30543
20.0	3.0	0.176471	-1.73460	0.73665	-0.30564

$\ln(\rho)$  is plotted against  $\ln(\tau)$  as shown in Fig (4.10).



**Fig. (4.9)** Plot of  $\ln(\rho)$  versus  $\ln(\tau)$  above the critical temperature for the critical mixture cyclohexane – phenol

The slope from Fig.(4.9) is  $x_\rho \nu = 0.0007$  and  $x_\rho$  equals 0.00109. The intercept equals  $\ln(\rho_0) = -0.3068$  which gives noncritical part  $\rho_0 = 0.7357 \frac{\text{gm}}{\text{cm}^3}$ .

Mass density typically exhibits power law behavior in the asymptotic region which are very close to a critical point like other thermodynamic properties. Mass density power law universal critical exponent, the value of critical exponent depending only on very general properties, such as dimensionality and the range of microscopic interactions in the system.

## Chapter Five

### Conclusion

The dynamic shear viscosity coefficients of the binary liquid mixture cyclohexane and phenol for different temperatures and concentrations are measured using glass capillary viscometer. Shear viscosity anomaly is clearly observed near the critical temperature  $T_c = 17.0^\circ\text{C}$  and the critical concentration  $x_c = 2.70\%$  by weight of phenol. Mode Coupling Theory of the dynamic shear viscosity is used to fit our experimental data above the critical temperature. It is found that the value of noncritical part of the dynamic shear viscosity  $\eta_0 = 0.8174$  cP. The mass density is expected power law, found the value of critical exponents  $x_\rho v = 0.0007$  and  $x_\rho$  equals 0.00109, and noncritical part of the mass density  $\rho_0 = 0.7357 \frac{\text{gm}}{\text{cm}^3}$ . The density of the critical mixture was measured to be  $\rho_c = 0.76271 \frac{\text{gm}}{\text{cm}^3}$ .

The critical isobaric specific heat  $c_{pc}$  for cyclohexane – phenol binary liquid mixture is determined to be  $106.6 \frac{\text{Joule}}{\text{Kg.K}}$ . The data of isobaric specific heat are used to determine the Joule's constant to be  $J = 4.1180 \frac{\text{Calorie}}{\text{Joule}}$ .

The isobaric thermal expansion coefficient  $\alpha_{pc}$  at the critical temperature and concentration of the critical mixture cyclohexane – phenol was calculated by using the two scale factor universality to be  $\alpha_{pc} = 1.66 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  and the background isobaric thermal expansion coefficient  $\alpha_{pb} = 5.87 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ .



The pressure derivation of the critical temperature along the critical line of cyclohexane – phenol binary  $T_c' = \frac{dT_c}{dP}$  is calculated and it is equals  $1.22 \times 10^{-4} \frac{K}{Pa}$ .

The results of the different thermodynamic properties of the binary liquid mixture cyclohexane – phenol that have been calculated or measured in Table (5.1).

**Table (5.1) Summary of the measured and calculated parameters in this work**

The measured and calculated value	Our results
$x_c^*$	2.70%
$T_c^*$	17.0°C
$\eta_0^{**}$	0.8174 cP
$c_{pc}^{**}$	106.6 $\frac{\text{Joule}}{\text{Kg} \cdot \text{K}}$
$J^{**}$	$J = 4.1180 \frac{\text{Calorie}}{\text{Joule}}$
$\alpha_{pc}^{**}$	$1.66 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$
$\alpha_{pb}^{**}$	$5.8701 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$
$x_{\rho v}^{**}$	0.0007
$x_{\rho}^{**}$	0.00109
$\rho_0^{**}$	$0.7357 \frac{\text{gm}}{\text{cm}^3}$
$\rho_c^*$	$0.7627 \frac{\text{gm}}{\text{cm}^3}$
$T_c'^{**}$	$1.22 \times 10^{-4} \frac{K}{Pa}$

\*: Measured value, \*\*: Calculated value

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جامعة النجاح الوطنية  
كلية الدراسات العليا

# السلوك الحرج لكثافة الخليط الثنائي السايكلوهكسان والفينول

إعداد

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قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في الفيزياء بكلية  
الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين.

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ب

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### الملخص

في هذا البحث تم قياس معامل اللزوجة للخليط الثنائي السايكلوهكسان - الفينول عند درجات حرارة و تراكيز مختلفة باستخدام مقياس اللزوجة الزجاجي الشعري. تم ملاحظة ظاهرة شذوذ اللزوجة عند درجة الحرارة ( $T_c = 17.0^\circ\text{C}$ ) والتركيز الحرج ( $x_c = 2.70\%$ ) من وزن الفينول. وتم تحليل النتائج فوق درجة الحرارة الحرجة باستخدام نظرية الازدواج. وايجاد قيمة الجزء غير الحرج من اللزوجة بالقرب من درجة الحرارة الحرجة لتكون ( $\eta_0 = 0.8174 \text{ cP}$ ). و اثبات سلوك الكثافة فوق درجة الحرارة الحرجة يتبع للقانون الآسي . ايجاد قيمة الجزء غير الحرج من الكثافة لتكون ( $\rho_0 = 0.7357 \frac{\text{gm}}{\text{cm}^3}$ ). و قد وجد ان معامل التمدد الحراري الحرج عند ثبات الضغط ( $\alpha_p$ ) ليكون ( $1.66 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ). ووجدت السعة الحرارية النوعية الحرجة عند ثبات الضغط ( $c_{pc}$ ) لتكون ( $106.6 \frac{\text{Joule}}{\text{kg.K}}$ ). ووجد ثابت جول ( J ) ( $4.1180 \frac{\text{Calorie}}{\text{Joule}}$ ) و قد تم ايجاد تغيير درجة الحرارة الحرجة بالنسبة للضغط  $T_c'$  ليكون ( $1.22 \times 10^{-4} \frac{\text{K}}{\text{Pa}}$ ).