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Two – Scale – Factor Universality of Binary Liquid Critical Mixture

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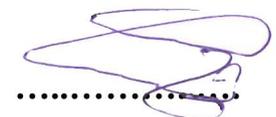
Dedication

To my mother, my father, my husband and my sister with respect and love…………..

Acknowledgment

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الإقرار

أنا الموقع/ة أدناه، الرسالة التي تحمل العنوان:

إشكاليات التنظيم الفني لوعاء الضريبة للإقرار بقانون بشأن الضريبة على الدخل رقم 8 لسنة 2011 وتعديلاته

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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.

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Table of Contents

VII

	References	37
	Appendix A	45
	Appendix B	47
	الملخص	ب

List of Tables

IX

List of Figures

List of Symbols and Abbreviations

T_c	Critical temperature
T	Absolute temperature
τ	Reduced temperature
x	Concentration by weight
x_c	Critical concentration by weight
c_P	Specific heat at constant pressure
c_{Pc}	Critical amplitude of specific heat at constant pressure
c_{Pb}	Background amplitude of specific heat at constant pressure
ρ	Mass density
ρ_c	Critical mass density
η	Dynamic viscosity
η_0	Noncritical part of viscosity
ξ	Correlation length
ξ_0	Critical amplitude of the correlation length
α_p	Isobaric thermal expansion coefficient
α_{pc}	Critical amplitude of isobaric thermal expansion coefficient
α_{pb}	Background amplitude of isobaric thermal expansion coefficient
q_D	Debye momentum cutoff
A	Constant of mode – coupling theory
$x_\eta \nu$	Critical exponent
ν	Critical exponent
α	Critical exponent
K_B	Boltzmann's constant
cP	Centipoise
R^+_ξ	Universal constant
T'_c	The pressure derivative of the critical temperature along the critical line

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Abstract

The dynamic shear viscosity of a binary liquid mixture phenol – water has been measured at different temperatures ($50.0°C \leq T \leq 75.0°C$) and different concentrations (0.00% up to 100.00% by weight of phenol). The critical temperature T_c and critical concentration x_c are found to be $67.0 \pm 0.1°C$ and 33.90% by weight of phenol respectively, the critical mass density ρ_c is measured to be 0.8952 ± 0.0001 g/cm^3.

The critical and background amplitudes of specific heat at constant pressure are calculated to be 78.12 J/kg.K and 85.29 J/kg.K respectively. The pressure derivative of the critical temperature along the critical line T_c' is calculated to be 9.722×10^{-6} K/Pa.

In addition, dynamic shear viscosity of binary liquid mixture phenol – cyclohexane has been measured at different temperatures
 ($14.0°C \leq T \leq 30.0°C$) and different concentrations (2.00% up to 39.70% by weight of phenol). The critical temperature T_c and critical concentration x_c are found to be $17.0°C$ and 2.70% by weight of phenol respectively, the critical mass density ρ_c is measured to be 0.7627 g/cm^3.

The critical and background amplitudes of isobaric thermal expansion coefficient α_{pc} and α_{pb} are calculated to be 8×10^{-6} K^{-1}, 6×10^{-4} K^{-1} respectively.

The pressure derivative of the critical temperature T_c' for the binary is calculated to be 2.8572×10^{-8} K/Pa.

The universal quantity R^+_ξ for the binary liquid critical mixture phenol – water is calculated to be 0.2716 ± 0.0005.

In addition, the universal quantity R^+_ξ for the binary liquid critical mixture phenol – cyclohexane is calculated to be 0.2699 ± 0.0001

The calculated values of the universal quantity R^+_ξ are in a good agreement with the theoretical value of R^+_ζ which is equal 0.2710.

The two binary liquid critical mixture belong to the class of universality "Two – Scale – Factor Universality".

Chapter One

Introduction

1.1 Binary Liquid Mixtures and Critical Point

Classification of materials depends on their composition, where matter may be classified as elements, compounds and mixtures.

Elements are the simplest form of a pure substance. Compounds are pure chemical substances composed of two or more different chemical elements (Brown *et al*, 2009; Hill *et al*, 2005; Whitten *et al*, 2000) that can be separated into simpler substances by chemical reactions (Wilbraham *et al*, 2002).

Mixtures are the product of a mechanical blending or mixing of chemical substances like elements and compounds, without chemical bonding or other chemical changes, so that each ingredient substance retains its own chemical properties (Atkins and De Paula, 2002).

Mixtures can be either homogeneous or heterogeneous. A homogeneous mixture is a type of mixture in which the composition is uniform and every part of the solution has the same properties. A heterogeneous mixture is a type of mixture in which the components can be seen, as there are two or more phases present.

Binary liquid mixtures are combination of two pure liquid substances, which have a limited solubility of each one in the other (Popiel, 1964).

Critical point is the point at which phase transition occurs at certain temperature called critical temperature and concentration (Cheung, 2011).

The critical point represents the boundary between regions of homogeneous and heterogeneous behavior in phase diagrams for mixtures (Gil *et al,* 2008).

Hypothesis of universality greatly reduces the variety of different types of critical behavior by classifying all systems into a small number of equivalence classes (Domb and Lebowitz, 1991).

The phenomenological theory of scaling has been extremely useful in understanding critical phenomena in model systems and in real materials (Domb and Lebowitz, 1991).

The first characteristic of a universality class is that all the systems have the same critical exponents. In addition, the equation of state, the correlation functions and other quantities become identical near criticality, provided one matches the scales of the order parameter, the ordering field, the correlation length and the correlation time (Domb and Lebowitz, 1991).

A property of hyper scaling or hyper universality (Two – Scale – Factor Universality) applies to systems in the universality classes of fluctuation-dominated (i.e. non-mean-field) critical behavior. These ideas were first developed phenomenologically and later confirmed by explicit renormalization group (RG) calculations (Domb and Lebowitz, 1991).

The RG theory of critical phenomena has elucidated the mathematical mechanism for scaling and universality, and has provided a number of calculational tools for estimating universal properties (Domb and Lebowitz, 1991).

1.2 Previous Studies

Greer and Hocken reported precise measurements of the density as a function of temperature in the one-phase region near the consolute point in nitroethane - 3-methylpentane. They found evidence of the critical anomaly in the thermal expansion, but were not able to determine a unique value for the critical exponent α. They performed computer experiments to determine under what conditions α could be extracted from thermal expansion data (Greer and Hocken, 1975).

Hohenberg and his group obtained the values of the universal ratios involving correlation length and specific-heat amplitudes from the ε expansion ($\varepsilon = 4$ - d, d: dimentionliy), for Ising, $X-Y$, and Heisenberg models. They defined the (transverse) correlation length in terms of the stiffness constant ρ_s (Hohenberg *et al*, 1976).

Thoen and his group measured the specific heat at constant pressure c_p along the line of the critical concentration for the binary system triethylamine - water as a function of temperature near the critical solution temperature at the critical concentration. They tested the Two $-$ Scale $-$ Factor Universality by combining the results of the amplitude of the specific heat singularity with the correlation length amplitude. The results strongly indicate that Two $-$ Scale $-$ Factor Universality is valid for binary systems (Thoen *et al*, 1977).

The shear viscosity as a function of molar composition and temperature of a binary mixture of aniline – cyclohexane have been measured. The results are analyzed in terms of the mode coupling theory (D'Arrigo *et al*, 1977).

Sengers supported the validity of the hypothesis of Two – Scale – Factor Universality for the correlation function of fluids near the gas – liquid critical point. He found that for Xe, SF_6, and CO_2 the dimensionless quantity R is universal and agrees with the value predicted by theory (Sengers, 1978).

Klein and Woermann calculated the critical part of specific heat at constant pressure and the coefficient of thermal expansion of binary liquid mixtures of critical composition from light – scattering data by using the Two – Scale – Factor Universality hypotheses of critical phenomena (Klein and Woermann, 1978).

Bloemen and his group investigated the anomaly in the specific heat at constant pressure c_p along the line of the critical concentration by means of a constant heating rate method. He obtained accurate results for $\tau = \frac{T - T_c}{T_c}$, values as small as 7×10^{-6}. Combining the amplitude of the correlation length with the critical amplitude of the specific heat allowed testing Two – Scale – Factor Universality (Bloemen *et al*, 1980).

The critical amplitude ξ_0 of the correlation length ξ has been experimentally determined for a wide variety of binary mixtures by using various techniques involving light scattering, x-ray scattering, turbidity, calorimetric and viscosimetric measurements (Beysens *et al*, 1982).

Sanchez and his group used a computerized high-resolution AC calorimetric technique to measure the heat capacity at constant pressure C_p of a critical 3-methylpentane - nitroethane binary liquid mixture. An analysis of these results yields universal parameters in good agreement

with those expected for the $d = 3, n = 1$ (Three-dimensional Ising) universality class (Sanchez *et al*, 1983).

Jacobs has measured the turbidity of the critical mixture methanol – cyclohexane above its critical point. The correlation length ξ was calculated using the Two – Scale – Factor Universality (Jacobs, 1986).

Thomson and his group had tested the protein – water system as a model for the study of phase transition and critical phenomena by measuring the critical temperature and concentration and different properties for the mixture (Thomson *et al*, 1987).

The critical amplitudes of the thermal expansion and specific heat at constant pressure have been calculated using the Two – Scale – Factor Universality relation for binary mixture nitrobenzene-n-hexane by Abdelraziq and his group. The Ultrasonic velocity and absorption as a function of temperature, concentration, and frequency (5–25 MHz) were measured. The shear viscosity as a function of concentration and temperature in the homogeneous phase above T_c was measured. The adiabatic coupling constant *g* was calculated and compared to the experimental value (Abdelraziq *et al*, 1990).

Refractive index and density have been obtained to determine thermodynamic divergences. The triethylamine – water mixture turbidity was measured to calculate the correlation length and compressibility values using the Two – Scale – Factor Universality by Zalczer and Beysens (Zalczer and Beysens, 1990).

Measurements of viscosity, ultrasonic velocity and absorption at the critical concentration as a function of temperature and frequency were made for the binary mixture of carbon tetrachloride – coconut oil by Abdelraziq and his group. Ultrasonic absorption at 5, 7, 10, 15, 21, 25, 30, and 35 MHz above T_c were analyzed by the dynamic scaling theory of Ferrell and Bhattacharjee (Abdelraziq *et al*, 1992).

Abdelraziq studied the ultrasonic absorption as a function of temperature and frequency for a binary mixture of cyclohexane – aniline. The results include that the absorption coefficient for the critical concentration increases as the critical temperature is approached from high temperature region for all frequencies (Abderaziq, 1996).

Heat capacity at constant pressure has been measured for the binary liquid mixture triethylamine – water. The critical exponent α was determined and the universality amplitude rate also was calculated based on the Two – Scale – Factor Universality by Flewelling and his group (Flewelling *et al*, 1996).

The ultrasonic absorption at 5, 7, 10, 15, 21 and 25 MHz, above critical temperature for a binary mixture of perfluomethyl – cyclohexane and carbon tetrachloride had been measured and analyzed by using the dynamic scaling theory. The values of $\frac{\alpha}{f^2}$ Vs. $f^{-1.06}$ are in good agreement with a theory (Abdelraziq, 2000).

Abdelraziq calculated the values of correlation length, adiabatic coupling constant and diffusion coefficient for the binary mixture aniline – cyclohexane using mode coupling theory (Abdelraziq, 2001).

Abdelraziq measured the shear viscosity coefficients of nitroethane – 3-methylpentane mixture using digital viscometer. The anomaly of shear viscosity was detected as a function of temperature and concentration. The results above the critical temperature T_c were analyzed by the mode coupling theory, the Debye momentum cutoff q_D and the constant A in the mode coupling approach were determined (Abdelraziq, 2002).

The universal quantity R^+_ζ of some binary liquid critical mixtures as methanol – cyclohexane, triethlamine – water, polystyrene – cyclohexane and others were calculated by Abdelraziq. He obtained the average value of $R^+_\zeta = 0.2691 \pm 0.0028$ which supports the theoretical value of $R^+_\zeta = \nu \left(\frac{n}{4\pi}\right)^{1/d}$ in three dimensions for n = 1 and d = 3, which indicates that fluid and binary mixtures transitions belong to the same class of universality (Abdelraziq, 2003).

Ultrasonic absorption and velocity measurements were made as a function of temperature for the binary mixtures of benzene – coconut oil and hexane - β, β' - chloroethyl ether . Ultrasonic absorption at 5, 7, 10, 15, 21, and 25 MHz and above T_c was analyzed by the dynamic scaling theory of Ferrell and Bhattacharjee (Abdelraziq, 2005).

The critical amplitude of the correlation length ξ_0 for three mixtures estimated by using the critical amplitude of the heat capacity in combination with the Two – Scale – Factor Universality (Souto-Caride *et al*, 2006).

The critical amplitude of the correlation length ξ_0 was determined via Two – Scale – Factor Universality, and the isobaric heat capacity for a set of

critical binary mixtures composed by an associated liquid and an alkane was measured (Souto-Caride *et al*, 2009).

Losada-Perez and his group used high-resolution adiabatic scanning calorimetry to study the specific heat capacity anomaly of the nitrobenzene – tetradecane mixture near its upper critical point. They derived the critical amplitude of the correlation length via Two – Scale –Factor Universality (Losada-Perez *et al,* 2010).

The ultrasonic velocity, viscosity and density were measured of n-hexane–alcohol binary liquid mixture. The acoustical parameters: adiabatic compressibility, free length and molar volume have been calculated. It is considered that the positive value of the excess volume represents the weak interaction between alcohols and n-hexane (Santhi *et al*, 2012).

The analytic function of Fixman's theory was modified in order to get an agreement with the experimental behavior of the binary liquid mixtures at critical concentration and above the critical temperature. Ultrasonic absorption and velocity of some binary liquid mixtures were used to test the validity of the Modified-Fixman's theory. It is found that the ratio of heat capacities (at constant pressure and volume) of the binary liquid mixtures is the term which plays the role to modify the Fixman's theory to get a good agreement with the experimental behavior (Qasem, 2014; Qasim and Abdelraziq, 2014).

Shear viscosity coefficients of benzene – coconut oil binary mixture have been measured using digital viscometer. The results above the critical temperature were analyzed by the mode coupling theory. The anomaly of

shear viscosity was detected as a function of temperature and concentration. Joule`s constant of benzene – coconut oil mixture (70% benzene by weight) was calculated by using Two – Scale – Factor Universality (Abdo, 2014; Abdo and Abdelraziq, 2014).

Kittany has measured the dynamic shear viscosity of the binary liquid mixture coconut oil - carbon tetrachloride. Debye parameter L was calculated using light scattering formula. The Debye momentum cutoff q_D and noncritical shear viscosity η_o were calculated using mode coupling theory (Kittany, 2014).

The dynamic shear viscosity of the binary liquid mixture methanol – cyclohexan for different temperatures and concentrations were measured using digital viscometer with UL adapter. The specific heat at constant pressure of the critical mixture methanol – cyclohexane was calculated using Two – Scale – Factor Universality (Omar, 2014; Omar and Abdelraziq, 2014).

1.3 Objectives

The aim of this study is to verify the value of the universal constant R^+_ζ for two binary liquid mixtures (phenol – water and phenol – cyclohexane) by applying the Two – Scale – Factor Universality principle.

The following physical properties of two binary liquid mixtures will be determined:

➢ critical temperate T_c

➢ critical concentration x_c

➢ Critical density ρ_c

➢ Critical and background amplitudes of specific heat c_{pc} and c_{pb} .

➢ Critical and background amplitudes of isobaric thermal expansion α_{pc} and α_{pb}.

➢ The pressure derivative of the critical temperature along the critical line T_c'

1.4 Layout

This thesis can be divided into five main chapters:

➢ **Chapter One** contains brief introduction to binary liquid mixtures, previous studies which are focusing on the properties of binary mixture and the objectives of the research.

➢ **Chapter Two** contains the definition of viscosity, the mode coupling theory and the shear viscosity of binary mixtures and the Two – Scale – Factor Universality hypotheses.

➢ **Chapter Three** contains brief description of the experimental apparatus, methodology of the experiment and procedure.

➢ **Chapter Four** displays the results and discussion of measured data, determining the critical temperature, concentration, density, specific heat at constant pressure, isobaric thermal expansion coefficient and calculating the pressure derivative of the critical temperature along the critical line and the universal constant $R^+{}_\xi$.

➢ **Chapter Five:** contains a list of conclusions about the two binary mixtures phenol – water and phenol – cyclohexane.

Chapter Two

Theory

2.1 Viscosity

The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress or tensile stress (Symon and Keith 1971). Viscosity is affected by different factors such as temperature, shear rate, catalyst, pressure, molecular weight concentration and storage age (Lide, 2005).

2.2 Mode Coupling Theory and Shear Viscosity of Binary Mixtures.

The mode coupling theory explains the behavior of the binary mixtures at the critical temperature and concentration.

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

$$\frac{\eta - \eta 0}{\eta} = \frac{\Delta \eta}{\eta} = A \ln \zeta + A \ln q_D, \qquad (2.1)$$

Where η_0 the noncritical part of the measured shear viscosity.

A is a constant which was calculated by D'Arrigo *et al* and given by A $\sim$ 0.054 (D'Arrigo *et* al, 1977), and q_D is Debye momentum cutoff.

The dynamic shear viscosity is temperature dependent at the critical concentration which is given by the power law (Klein and Woermann, 1978; Abdalraziq, 2002).

$$\eta = \eta_0 \ \tau^{-x_\eta \nu} \qquad (2.2)$$

Where t is the reduced temperature $\tau = \frac{T-T_c}{T_c}$, x_η and ν are critical exponents where $x_\eta \nu = 0.04$ (D'Arrigo *et al*, 1977; Klein and Woermann, 1978).

2.3 Two – Scale – Factor Universality

The Two – Scale – Factor Universality has been used in modern theories to explain the critical phenomena of binary liquid mixtures by predicting R_ζ (Hohenberg *et al*, 1976).

The Two – Scale – Factor Universality hypothesis states that the critical amplitudes do not depend on three different scales of parameter (length, temperature, external field) but only on two scales of parameter (Bervillier and Godreche, 1980). Most of the observed quantities depend only on the dimensionalities of the space (d) and of the order parameter (n) (Zalczer *et al,* 1983)

Stautfer, Ferer and Wortis generalized the concept of thermodynamic universality by the hypothesis of Two – Scale – Factor Universality for correlation functions. This hypothesis states that the correlation function of the system is determined near the critical point (Stautfer *et al*, (1972).

The renormalization group theory provides a method for proving scaling relations, and for calculating exponents and universal amplitude ratios as expansions in $\varepsilon = 4 - d$ or $1/n$, where d is the dimensionality and n is the order parameter (Hohenberg *et al*, 1976).

Wilson's expansion methods used in the verification of Two – Scale – Factor Universality to second order in ε (Aharony, 1974).

The fluid and binary mixtures transitions belong to the same class of universality d = 3, n = 1(Abdelraziq, 2003) .

All binary liquid mixtures with critical mixing points belong to the same universality class. The universality concept offers the possibility to relate critical amplitudes of these systems. The exponents are universal and related by the so-called scaling laws (Abdelraziq, 2003).

The amplitudes of the correlation length, thermal expansion and specific heat can be deduced using the universal amplitude combinations. (Zalczer *et al*, 1983; Clerke *et al*, 1983; Jacobs, 1986; Bloemen, *et al*, 1980).

Correlation length is a measure of the distances over which the spin–spin (or density–density) correlations in the system extend (Pathria and Beale, 2011).

The correlation length of a binary mixture at critical composition exhibits an anomalous behavior conforming to the following exponential law:

$$\xi = \xi^+_0 \ \tau^{-\nu}, \qquad T > T_c \qquad (2.3)$$

Where ν is a critical exponent which accepted to be 0.630 ± 0.001, ξ^+_0 is the critical amplitude and t is the reduced temperature $\tau = \frac{T - T_c}{T_c}$, where T_c is the critical temperature (Souto-Caride *et al*, 2006).

The specific heat at constant pressure c_p in zero field is singular and is given by:

$$c_p = c^+_{pc} \ \tau^{-\alpha} + c^+_{pb} \ , \qquad T > T_c \qquad (2.4)$$

Where c_{pc} and c_{pb} are the critical and background amplitudes of the specific heat and $\alpha = 0.11$ is the critical exponent (Bhattacharjee and Ferrell, 1981; Abdelraziq, 2003; Iwanowski, 2007; Bhattacharjee *et al*, 2010).

The asymptotic behavior of the thermal expansion α_p can be represented by power law of the form,

$$\alpha_p = \alpha^{+}_{pc}\, \tau^{-\alpha} + \alpha^{+}_{pb}\,, \qquad T > T_c \qquad (2.5)$$

Where α_{pc} and α_{pb} are the critical and the background amplitudes of the thermal expansion (Abdelraziq, 2003).

With these three amplitudes $\xi^{+}_{0,}$ $c^{+}_{pc,}$ and $\alpha^{+}_{pc,}$ it is possible to construct a quantity, denoted R^{+}_{ζ}, which is universal in the same sense as critical indices are universal. This quantity is defined as:

$$R^{+}_{\xi} = \xi_0 \left(\frac{\alpha\, c_{pc}\, \rho_c}{K_B}\right)^{1/d} = \xi_0 \left(\frac{\alpha\, T_c\, \alpha_{pc}}{T'_c\, K_B}\right)^{1/d} \qquad (2.6)$$

Where $d = 3$ is the dimension of the space, K_B is Boltzman's constant, ρ_c is the density of the critical mixture at critical temperature T_c and concentration $T'_c = \frac{dT_c}{dp}$ is the pressure derivative of the critical temperature along the critical line (Abdelraziq, 2003).

The theoretical value of the universal constant $R^{+}_{\xi} = \nu \left(\frac{n}{4\pi}\right)^{1/d}$ in three dimensions for $n = 1$, $d = 3$ and $\nu = 0.64$ which equal 0.2710 (Abdelraziq, 2003).

Chapter Three

Methodology

In this work two binary mixtures were used the phenol – water binary mixture and phenol – cyclohexane binary mixture. The viscosities were measured for both at different temperatures and concentrations. The critical temperature, concentration, heat capacity at constant pressure and density were measured of each mixture.

3.1 Experimental Apparatus

3.1.1 Capillary Viscometer: is a device used to measure the viscosity of the liquid with a known density by measuring the time for a known volume of the liquid (the volume contained between the marks in Fig.(3.1)) to flow through the capillary under the influence of gravity(Generalic and Eni**,** 2014).
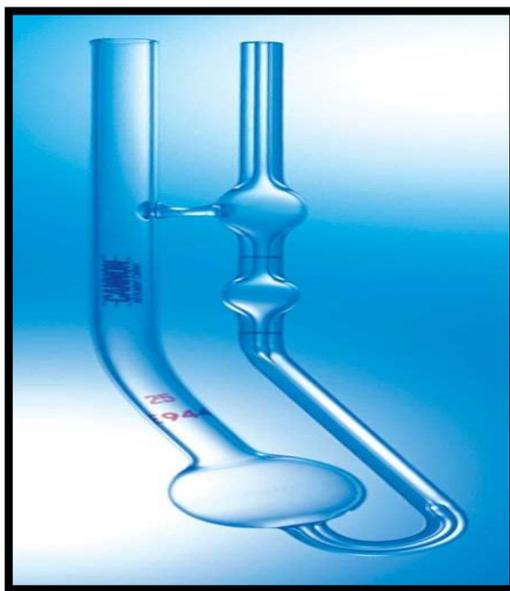
Fig. (3.1): Capillary viscometer

The capillary viscometer is used to calculate the viscosities of the mixtures by this law

$$\eta_1 = \eta_2 \frac{\rho_1 t_1}{\rho_2 t_2} \qquad (3.1)$$

Where η_1 is the viscosity of the mixture, η_2 is the viscosity of the water, ρ_1 and ρ_2 are the densities of the mixture and the water respectively.

t_1 and t_2 are the time needed to flow from the mark points in the capillary of the mixture and the water respectively (Generalic and Eni, 2014).

3.1.2 Brookfield Digital Viscometer Model DV-I+:

It measures the viscosity of a liquid in centipoises with accuracy $\pm 1\%$. It is used to measure the dynamic viscosity from 1 up to $1.33 \times 10^7 \, cP$ with accuracy $\mp 1\%$ (Fig. (3.2)). It consists of a set of seven spindles (RVSPINDLE SET) and UL-ADAPTER. The rotational speeds of the spindles are two set. The first is: 0.0, 0.3, 0.6, 1.5, 3, 6, 12, 30, 60RPM and the second set is: 0.0, 0.5, 1, 2, 2.5, 4, 5, 10, 20, 50, 100 RPM (Brookfield manual, 1999).

This viscometer is used to measure the viscosity of pure phenol sample with temperature range from (50-75) ^{0}C.

Fig.(3.2): Brookfield Digital Viscometer Model DV-I+

3.1.3 Digital Prima Long Thermometer:

This instrument (Fig.(3.3)) is used to measure the temperature, its range is from -20 ^{0}C up to 100 ^{0}C and accuracy ± 1%.

Fig.(3.3): Digital Prima Long Thermometer

3.1.4 Julabo F25-MV Refrigerated and Heating Circulator:

It is used to control the temperature of the sample, with accuracy ±1%, which is shown Fig.(3.4).

Fig.(3.4): Julabo F25-MV Refrigerated and Heating Circulator

3.1.5 The Analytical Balance HR-200:

It is used to measure the mass in gm unit with accuracy of ± 0.00005% which is shown in Fig.(3.5).

Fig.(3.5): The Analytical Balance HR-200

3.1.6 Pycnometer:

A 10 ml pycnometer which is shown in Fig.(3.6) is used to measure the mass density of the mixtures and pure substances using

$$\rho = \frac{mass\ of\ the\ liquid}{10\ ml} \tag{3.2}$$

Where ρ in g/cm^3.

Fig.(3.6): Pycnometer

3.1.7 Calorimeter:

The calorimeter is an instrument used to measure the heat released during chemical reactions or physical changes as well as heat capacity. A calorimeter has been constructed with glass pyrex beaker instead of the

aluminum, and a nichrome resistance wire covered by a U- tube glass as in Fig.(3.7), this calorimeter has been constructed to avoid the reaction of phenol with metals

Fig.(3.7): Calorimeter

3.1.8 The Calorimeter Set Up

The Calorimeter set up which is shown in Fig.(3.8) contains digital voltmeter with accuracy in the DC volts range ±1 % and digital ammeter with accuracy ±1 % and power supply and thermometer.

Fig.(3.8): Calorimeter set up

3.2 Samples Preparation and the Procedure:

The densities of pure substances phenol, water, and cyclohexane are measured using the pycnometer.

Samples prepared for the binary liquid mixture phenol – water in different concentrations by weight of phenol from (0.00% to 100.00% by weight of phenol), and from (2.00% to 39.70 by weight of phenol) for the binary liquid mixture phenol – cyclohexane.

The concentration of phenol by weight in the binary mixture is:

$$X_{\text{phenol}} = \frac{\rho\,phenol * V\,phenol}{\rho\,phenol * V\,phenol + \rho\,water * V\,water} \qquad (3.3)$$

The viscosity of the mixtures phenol – water and phenol – cyclohexane is calculated using (3.1) relation; by taking the time of flow of each concentration twice and taking the average at different temperatures.

The viscosity is plotted as a function of temperature of each concentration to find the critical temperature and the critical concentration.

The specific heat is measured by cooling method for the binary mixture phenol – water at the critical concentration and above the critical temperature.

The specific heat at constant pressure c_p is calculated using the following relation :

$$W = I\,V\,t = (m_r\,c_r + m_b\,c_b + m_g\,c_g + m_p\,c_p)\,\Delta T \qquad (3.4)$$

W : is the work in joule, I : is the current in Ampere, V : is the voltage in volt, t : is the time in Second and ΔT is the temperature difference.

m_p : is the mass of the binary mixture, c_p : is the binary mixture specific heat.

m_r : is resistance wire mass = 0.8800g, c_r : is the resistance wire specific heat = 0.45 J/g.K.

m_p : is the mass of the pyrex beaker = 81.2520g, c_p : is the pyrex beaker specific heat = 0.75J/g.K.

m_g : is the mass of the glass U-tube = 15.0390g, c_g : is the glass U-tube specific heat = 0.84 J/g.K.

The specific heat for the binary mixture phenol – water is plotted as a function of $\tau^{-\alpha}$ to determine the critical amplitude of specific heat at constant pressure c_{pc}.

Chapter Four

Results and Discussion

4.1 Viscosity Measurements

❖ Phenol – Water Binary Mixture

The results of the dynamic viscosity η as a function of temperature for different concentrations of phenol – water   binary mixture are given in Table A.1 in appendix A. The dynamic shear viscosities of phenol – water binary mixture are plotted as a function of temperature at different concentrations of phenol in appendix B.
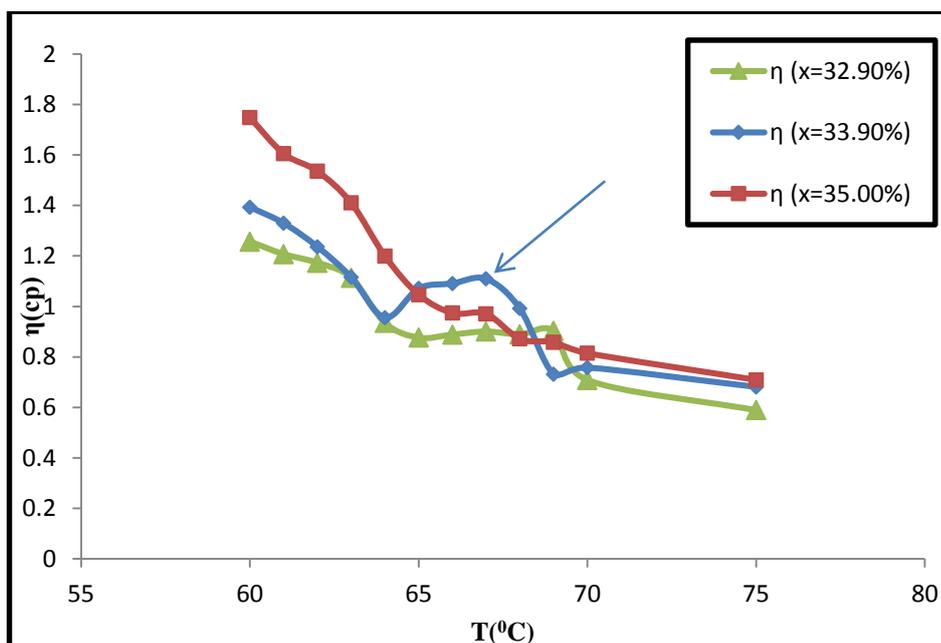
Fig. (4.1) The dynamic shear viscosity of phenol – water mixture as a function of temperature at concentrations 32.90%, 33.90% and 35.00% by weight of phenol.

The critical temperature occurs when the two phases of the binary mixture become one phase which appears as anomaly at 67.0 ^{0}C for the concentration 33.90% by weight of phenol, as shown in Fig.(4.1).

In addition, the mixture was visually observed as one phase at the critical temperature and concentration.

❖ **Phenol – Cyclohexane Binary Mixture**

The results of the dynamic viscosity η as a function of temperature for different concentrations of phenol – cyclohexane binary mixture are given in Table A.2 in appendix A. The dynamic shear viscosities of phenol – cyclohexane binary mixture are plotted as a function of temperature at different concentrations of phenol in appendix B.
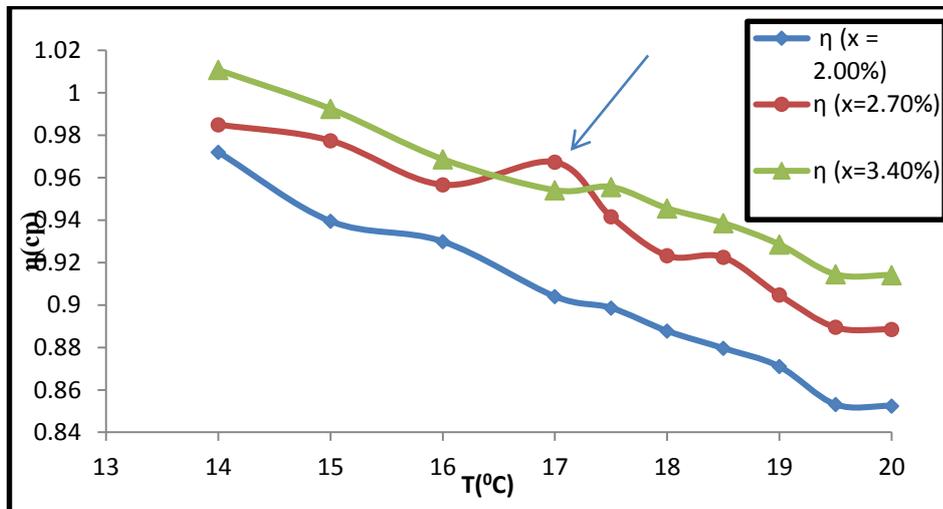
Fig. (4.2) The dynamic shear viscosity of phenol – cyclohexane mixture as a function of temperature at concentrations 2.00%, 2.70% and 3.40% by weight of phenol**.**

The critical temperature occurs when the two phases of the binary mixture become one phase which appears as anomaly at 17.0 ^{0}C for the concentration 2.70 % by weight of phenol, as shown in Fig.(4.2).

In addition, the mixture was visually observed as one phase at the critical temperature and concentration.

The behavior of viscosity as shown in appendix B figures show that at each concentration of the phenol – water and phenol – cyclohexane binary mixtures the dynamic viscosity decreases as the temperature increase. This because when the temperature increases, the time of interaction between neighboring molecules of a mixture decreases because of the increased velocities of individual molecules. The macroscopic effect is that the intermolecular force appears to decrease so the viscosity decreases, and the viscosity increase with increasing concentration of phenol because the phenol is more viscous than water and cyclohexane.

4.2 Mass Density Measurements

❖ **Phenol – Water Binary Mixture**

The results of the mass density ρ as a function of temperature for different concentrations of phenol – water binary mixture are given in Table 4.1 and Table 4.2.

Table (4.1) The mass density measurements at different temperatures and concentrations (0.00% - 35.00% by weight of phenol) for the binary liquid mixture phenol – water.

T (°C)	$\rho(\frac{g}{cm^3})$ 0.00%	$\rho(\frac{g}{cm^3})$ 10.17%	$\rho(\frac{g}{cm^3})2$ 0.80%	$\rho(\frac{g}{cm^3})3$ 0.20%	$\rho(\frac{g}{cm^3})3$ 1.80%	$\rho(\frac{g}{cm^3})3$ 2.90%	$\rho(\frac{g}{cm^3})3$ 3.90%	$\rho(\frac{g}{cm^3})3$ 5.00%
50.0	0.9880	0.9770	0.9210	0.9650	0.9839	0.9524	0.9610	1.0721
55.0	0.9851	1.0008	0.9427	0.9580	0.9820	0.9464	0.9524	1.0740
57.0	0.9847	0.9670	0.9236	0.9653	0.9914	0.9410	0.9876	1.0531
58.0	0.9842	0.9783	0.9481	0.9707	0.9510	0.9563	1.0065	1.0611
59.0	0.9837	0.9752	0.9477	0.9650	1.000	0.9364	0.9531	1.0795
60.0	0.9832	0.9880	0.9303	0.9786	0.9950	0.9452	0.9519	1.0680
61.0	0.9826	0.9805	0.9322	0.9775	0.9920	0.9375	0.9438	1.0555
62.0	0.9821	0.9770	0.9229	0.9712	0.9840	0.9386	0.9333	1.0555
63.0	0.9816	0.9758	0.9488	0.9710	0.9890	0.9469	0.9225	1.0555
64.0	0.9810	0.9708	0.9565	0.9820	0.9860	0.9445	0.9137	1.0555
65.0	0.9805	0.9775	0.9648	0.9726	0.9610	0.8975	0.9180	0.9368
66.0	0.9800	0.9878	0.9741	0.9828	0.9860	0.9471	0.9208	0.9368
67.0	0.9790	0.9860	0.9452	0.9750	0.9890	0.9318	0.8952	0.9368
68.0	0.9789	0.9830	0.9660	0.9676	0.9920	0.9257	0.8973	0.9368
69.0	0.9780	0.9804	0.9542	0.9621	0.9850	0.9215	0.9260	0.9368
70.0	0.9777	0.9243	0.9430	0.9448	0.9750	0.8542	0.9549	0.9325
75.0	0.9748	0.9860	0.9521	0.9478	0.9690	0.8912	0.9520	0.9435

Table (4.2) The mass density measurements at different temperatures and concentrations (37.10% - 100.00% by weight of phenol) for the binary liquid mixture phenol – water.

T (°C)	$\rho(\frac{g}{cm^3})$ 37.10%	$\rho(\frac{g}{cm^3})40$ .20%	$\rho(\frac{g}{cm^3})$ 49.80%	$\rho(\frac{g}{cm^3})$ 59.79%	$\rho(\frac{g}{cm^3})$ 70.40%	$\rho(\frac{g}{cm^3})$ 79.77%	$\rho(\frac{g}{cm^3})$ 89.90%	$\rho(\frac{g}{cm^3})$ 100.00%
50.0	0.9606	0.9593	1.0253	1.0158	0.9890	1.0322	1.0284	1.0534
55.0	0.9539	0.9602	1.0193	1.0151	1.0061	1.0281	1.0317	1.0527
57.0	0.9601	0.9658	0.9667	1.0161	1.0059	1.0250	1.0352	1.0521
58.0	0.9545	0.9555	1.0079	1.0108	0.9978	1.0174	1.0293	1.0514
59.0	0.9504	0.9554	0.9980	1.0027	0.9928	1.0223	1.0335	1.0552
60.0	0.9559	0.9542	0.9869	0.9900	0.9972	1.0169	1.0316	1.0242
61.0	0.9491	0.9471	0.9871	0.9814	1.0045	1.0769	1.0355	1.0229
62.0	0.9384	0.9591	0.9921	0.9718	1.0095	1.0312	1.0343	1.0317
63.0	0.9566	0.9451	0.9865	0.9686	1.0126	1.0238	1.0327	1.0305
64.0	0.9629	0.9495	0.9748	0.9725	1.0001	1.0226	1.0338	1.0295
65.0	0.9543	0.9558	0.9889	0.9607	0.9913	1.0168	1.0324	1.0294
66.0	0.9370	0.9478	0.9750	0.9667	1.0017	1.0175	1.0301	1.0285
67.0	0.9396	0.9378	0.9760	0.9700	0.9935	1.0117	1.0341	1.0374
68.0	0.9462	0.9331	0.9666	0.9640	1.0012	1.0206	1.0274	1.0367
69.0	0.9253	0.9301	0.9786	0.9738	1.0003	1.0114	1.0286	1.0357
70.0	0.9290	0.9364	0.9825	0.9612	0.9993	1.0164	1.0275	1.0493
75.0	0.9510	0.9390	0.9648	0.9835	0.9977	1.0183	1.0261	1.0484

The critical mass density $\rho_c = 0.8952$ g/cm^3 $\pm$ 0.0001 at the critical concentration $x_c = 33.90\%$ by weight of phenol and the critical temperature $T_c = 67.0\ ^0$C for the binary mixture phenol – water.

❖ **Phenol – Cyclohexane Binary Mixture**

The results of the mass density ρ as a function of temperature for different concentrations of phenol – cyclohexane binary mixture are given in Table 4.3 and Table 4.4.

Table (4.3) The mass density measurements at different temperatures and concentrations (2.00% - 16.00% by weight of phenol) for the binary liquid mixture phenol – cyclohexane.

T (°C)	$\rho\left(\frac{g}{cm^3}\right)$ 2.00%	$\rho\left(\frac{g}{cm^3}\right)$ 2.70%	$\rho\left(\frac{g}{cm^3}\right)$ 3.40%	$\rho\left(\frac{g}{cm^3}\right)$ 6.70%	$\rho\left(\frac{g}{cm^3}\right)$ 9.90%	$\rho(\frac{g}{cm^3})$ 13.20%	$\rho\left(\frac{g}{cm^3}\right)$ 16.00%
14.0	0.7307	0.7381	0.7430	0.7467	0.7535	0.7591	0.7844
15.0	0.7304	0.7382	0.7427	0.7462	0.7532	0.7585	0.7840
16.0	0.7302	0.7379	0.7425	0.7460	0.7531	0.7584	0.7831
17.0	0.7298	0.7627	0.7423	0.7457	0.7529	0.7581	0.7827
17.5	0.7296	0.7376	0.7424	0.7454	0.7527	0.7578	0.7825
18.0	0.7294	0.7374	0.7418	0.7452	0.7525	0.7576	0.7823
18.5	0.7290	0.7372	0.7416	0.7450	0.7524	0.7574	0.7821
19.0	0.7288	0.7370	0.7414	0.7447	0.7521	0.7572	0.7819
19.5	0.7286	0.7368	0.7412	0.7445	0.7519	0.7568	0.7817
20.0	0.7283	0.7367	0.7410	0.7444	0.7517	0.7571	0.7816
20.5	0.7282	0.7364	0.7407	0.7440	0.7515	0.7563	0.7813
21.0	0.7278	0.7359	0.7406	0.7437	0.7513	0.7558	0.7807
22.0	0.7276	0.7357	0.7403	0.7435	0.7509	0.7558	0.7805
25.0	0.7272	0.7352	0.7396	0.7426	0.7504	0.7549	0.7800
30.0	0.7266	0.7344	0.7387	0.7418	0.7497	0.7542	0.7792

Table (4.4) The mass density measurements at different temperatures and concentrations (17.90% - 39.70% by weight of phenol) for the binary liquid mixture phenol – cyclohexane.

T (°C)	$\rho\left(\frac{g}{cm^3}\right)$ 17.90%	$\rho\left(\frac{g}{cm^3}\right)$ 19.46%	$\rho\left(\frac{g}{cm^3}\right)$ 22.50%	$\rho\left(\frac{g}{cm^3}\right)$ 25.50%	$\rho(\frac{g}{cm^3})$ 31.00%	$\rho\left(\frac{g}{cm^3}\right)$ 34.19%	$\rho\left(\frac{g}{cm^3}\right)$ 37.00%	$\rho\left(\frac{g}{cm^3}\right)$ 39.70%
14.0	0.7739	0.7628	0.7845	0.7988	0.7997	0.8119	0.8269	0.8310
15.0	0.7739	0.7627	0.7842	0.7982	0.7991	0.8114	0.8265	0.8308
16.0	0.7739	0.7625	0.7839	0.7979	0.7987	0.8109	0.8260	0.8306
17.0	0.7737	0.7624	0.7834	0.7977	0.7986	0.8107	0.8256	0.8303
17.5	0.7734	0.7616	0.7829	0.7976	0.7984	0.8106	0.8253	0.8301
18.0	0.7734	0.7615	0.7827	0.7972	0.7982	0.8102	0.8250	0.8300
18.5	0.7732	0.7613	0.7825	0.7968	0.7980	0.8099	0.8247	0.8297
19.0	0.7729	0.7615	0.7825	0.7966	0.7978	0.8096	0.8243	0.8295
19.5	0.7729	0.7609	0.7821	0.7963	0.7976	0.8092	0.8241	0.8290
20.0	0.7726	0.7607	0.7819	0.7963	0.7974	0.8089	0.8236	0.8288
20.5	0.7724	0.7605	0.7814	0.7959	0.7977	0.8085	0.8233	0.8284
21.0	0.7722	0.7603	0.7810	0.7957	0.7969	0.8082	0.8229	0.8281
22.0	0.7719	0.7598	0.7801	0.7953	0.7967	0.8079	0.8226	0.8278
25.0	0.7717	0.7593	0.7802	0.7946	0.7962	0.8075	0.8221	0.8274
30.0	0.7698	0.7590	0.7797	0.7939	0.7959	0.8071	0.8213	0.8265

The critical mass density $\rho_c = 0.7627$ g/cm³ $\pm$ 0.0001 at the critical concentration $x_c = 2.70\%$ by weight of phenol and the critical temperature $T_c = 17.0\ ^0C$ for the binary mixture phenol – cyclohexane.

4.3 Specific Heat Measurements

❖ **Phenol – Water Binary Mixture**

The specific heat at constant pressure c_p for the binary mixture phenol–water is calculated using the relation:

$$W = I\,V\,t = (m_r\,c_r + m_b\,c_b + m_g\,c_g + m_p\,c_p)\,\Delta T$$

The specific heat at constant pressure is given by relation (2.4) which is

$$c_p = c^+_{pc}\,\tau^{-\alpha} + c^+_{pb} \qquad (2.4)$$

Where t is the reduced temperature and α is the critical exponent which equals 0.11.

The specific heat at constant pressure and $\tau^{-\alpha}$ at different temperatures are presented in Table (4.5).

Table (4.5) Specific heat data of binary mixture phenol – water.

Temperature (^{0}C)	$\dfrac{T - T_c}{T_c}$	$\tau^{-\alpha}$	c_p (J/kg.K)
68.0	0.014925	1.588065	30.4
68.5	0.022388	1.518792	29.9
69.0	0.029851	1.471482	29.4
69.5	0.037313	1.435803	28.6
70.0	0.044776	1.407294	27.2
71.0	0.059701	1.363458	23.5
72.0	0.074627	1.330398	19.5
73.0	0.089552	1.303982	16.4
74.0	0.104478	1.282057	13.7
75.0	0.119403	1.263364	10.9

The specific heat at constant pressure is plotted with $\tau^{-\alpha}$ in Fig.(4.3), using the relation

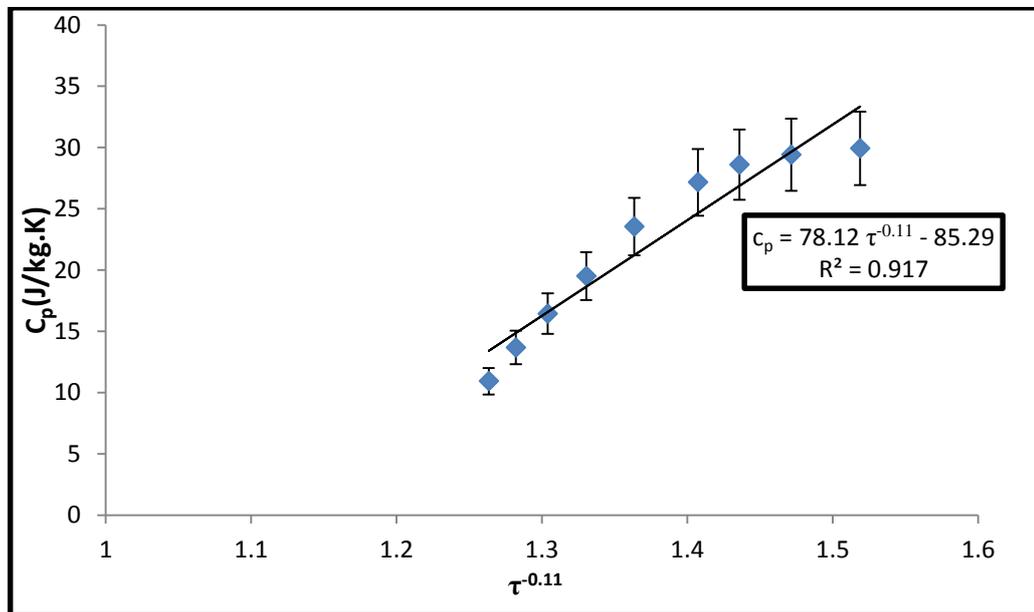$$c_p = c^+_{pc}\,\tau^{-\alpha} + c^+_{pb}$$

Fig. (4.3) The specific heat at constant pressure c_p versus $\tau^{-0.11}$ for binary mixture phenol – water

The slope of the line is $c_{pc} = 78.12 \pm 0.04$ J/kg.K, which is the critical amplitude of specific heat at constant pressure of the binary mixture phenol – water, and the intercept is $c_{pb} = 85.29 \pm 0.04$ J/kg.K which is the background amplitude of specific heat at constant pressure.

4.4 Calculation of The Universal Quantity R^+_{ξ}

The Two – Scale – Factor Universality relation (2.6),

$$R^+_{\xi} = \xi_0 \left(\frac{\alpha\, c_{pc}\, \rho_c}{K_B} \right)^{1/d} = \xi_0 \left(\frac{\alpha\, T_c\, \alpha_{pc}}{T'_c\, K_B} \right)^{1/d} \qquad (2.6)$$

The universal quantity R^+_{ξ} can be calculated using the first term

$$R^+_{\xi} = \xi_0 \left(\frac{\alpha\, c_{pc}\, \rho_c}{K_B} \right)^{1/d}$$

Where the critical exponent $\alpha = 0.11$, Boltzmann's constant $K_B = 1.38 \times 10^{-23}$ J/K, and the dimensionality $d = 3$.

❖ **Phenol – Water Binary Mixture**

The universal quantity R^+_{ξ} can be calculated for the binary mixture phenol – water to be 0.2716 ± 0.0005 by substituting the values of c_{pc} = 78.12 J/kg.K, $\rho_c = 0.8952$ gm/cm³, and $\xi_0 = 3.3$Å (Abdelraziq, 2015). The theoretical value of $R^+_{\zeta} = v \left(\frac{n}{4\pi} \right)^{1/d}$ in three dimensions for n = 1, d = 3 and $v = 0.64$, equal 0.2710.

❖ **Phenol – Cyclohexane Binary Mixture**

The universal quantity R^+_{ξ} can be calculated for the binary mixture phenol – cyclohexane to be 0.2699 ± 0.0001 by substituting the values of c_{pc} = 106.60 J/kg.K (Hussien, 2015), $\rho_c = 0.7627$ gm/cm³, and $\xi_0 = 3.12$Å (Abdelraziq, 2015). The theoretical value of $R^+_{\zeta} = 0.2710$.

This indicates that the two binary liquid critical mixtures phenol – water and phenol – cyclohexane belong to the same class of universality "Two – Scale – Factor Universality".

4.5 Calculation of T'_c

The Two – Scale – Factor Universality relation (2.6),

$$R^+_\xi = \xi_0 \left(\frac{\alpha \, c_{pc} \, \rho_c}{K_B} \right)^{1/d} = \xi_0 \left(\frac{\alpha \, T_c \, \alpha_{pc}}{T'_c \, K_B} \right)^{1/d} \qquad (2.6)$$

The pressure derivative of the critical temperature along the critical line T'_c can be calculated using the second term

$$R^+_\xi = \xi_0 \left(\frac{\alpha \, T_c \, \alpha_{pc}}{T'_c \, K_B} \right)^{1/d}$$

❖ **Phenol – Water Binary Mixture**

   The pressure derivative of the critical temperature along the critical line T'_c for the binary mixture phenol – water can be calculated to be 9.722 $\times 10^{-6}$ K/Pa. The values of $T_c = 340$ K, $\alpha_{pc} = 0.002$ K^{-1} (Reehan, 2015), $\xi_0 = 3.3$Å (Abdelraziq, 2015) and $R^+_\xi = 0.2716$.

❖ **Phenol – Cyclohexne Binary Mixture**

   The critical amplitude of isobaric thermal expansion coefficient α_{pc} is need to calculate T'_c.

   The isobaric thermal expansion coefficient α_p can be calculated using the relation:

$$\alpha_p = \frac{1}{V} \left(\frac{dV}{dT} \right)_p \qquad (4.1)$$

Where V: is the volume, T: is the temperature and P : is the pressure.
Equation 4.1 could be expressed in another form by applying $V = \frac{m}{\rho}$.

$$\alpha_p = -\frac{1}{\rho}\left(\frac{d\rho}{dT}\right)_p = \alpha_p = \rho\left(\frac{d\rho^{-1}}{dT}\right) \tag{4.2}$$

Where, m : is the mass and ρ: is the density of the binary mixture.

The values of the density and its reciprocal at different temperatures above the critical point are presented in Table (4.6).

Table (4.6): The mass density and its reciprocal values at different temperatures for the binary mixture phenol – cyclohexane.

T(K)	Mass density ρ(gm/cm³)	ρ^{-1}(cm³/gm)
290.5	0.7376	1.3561
291.0	0.7374	1.3565
291.5	0.7372	1.3568
292.0	0.7370	1.3572
292.5	0.7368	1.3574
293.0	0.7367	1.3579
293.5	0.7364	1.3589
294.0	0.7359	1.3592
295.0	0.7357	1.3602
298.0	0.7352	1.3616

The reciprocal of the density is fitted with the corresponding temperatures and the slope $\left(\frac{d\rho^{-1}}{dT}\right)$ is determined from Fig.(4.4).
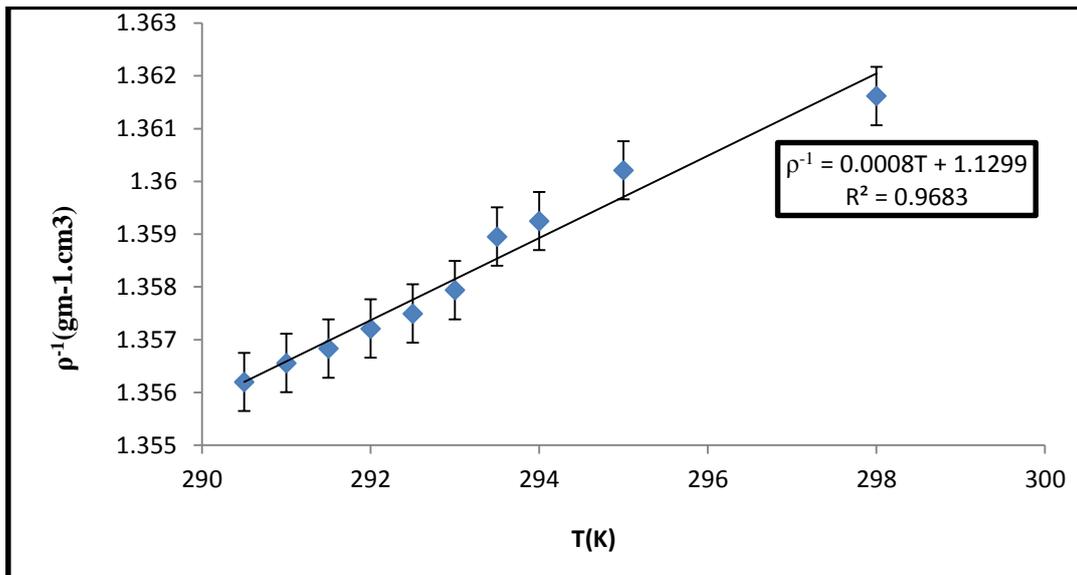
Fig.(4.4) The reciprocal of density for the binary mixture phenol – cyclohexane   as a function of temperature

The slope from Fig.(4.5) is $\dfrac{d\rho^{-1}}{dT} = 0.0008 \ \dfrac{cm^3}{g.K}$.

The critical and the background isobaric thermal expansion coefficients can be determined by linear fitting of the isobaric thermal expansion coefficient α_p versus $\tau^{-\alpha}$, where $\tau = \dfrac{T - T_c}{T_c}$ and $\alpha = 0.11$ depending on the relation:

$$\alpha_p = \alpha_{pc}\tau^{-\alpha} + \alpha_{pb} \tag{2.4}$$

The values of α_p are calculated using equation (4.2) and the data are presented in Table (4.7).

Table (4.7) The isobaric thermal expansion coefficient at different temperatures for the critical mixture of phenol – cyclohexane

T(K)	$\alpha_p(K^{-1})$	$\tau^{-0.11}$
292.0	0.000589	1.728823
292.5	0.000589	1.686904
293.0	0.000589	1.65341
293.5	0.000589	1.62561
294.0	0.000589	1.601907
295.0	0.000588	1.563065
298.0	0.000588	1.484307

The data of the isobaric thermal expansion coefficient α_p are plotted versus $\tau^{-0.11}$ as shown in Fig.(4.5).
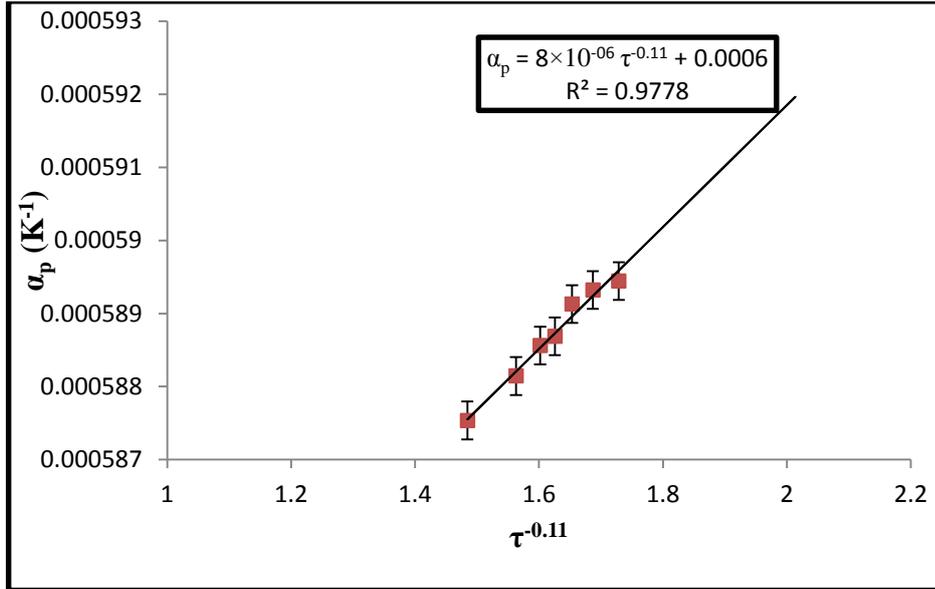
Fig.(4.5) The isobaric thermal expansion coefficient for the binary mixture phenol – cyclohexane as a function of $\tau^{-0.11}$.

The slope of the line represents the critical isobaric thermal expansion coefficient $\alpha_{pc} = 8 \times 10^{-6}$ K^{-1}, and the intercept of the line represents the background isobaric thermal expansion coefficient $\alpha_{pb} = 6 \times 10^{-4}$ K^{-1}.

The pressure derivative of the critical temperature along the critical line T_c' for the binary mixture phenol – cyclohexane is calculated to be 2.8572×10^{-8} K/Pa. The values of $T_c = 290$ K, $\alpha_{pc} = 6 \times 10^{-6}$ K^{-1}, $\xi_0 = 3.12$Å (Abdelraziq, 2015) and $R^{+}_{\xi} = 0.2699$.

Chapter Five

Conclusion

The dynamic shear viscosity of two binary liquid mixtures phenol – water and phenol – cyclohexane has been measured at different temperatures and concentrations.

The critical temperature and critical concentration for the binary liquid mixture phenol – water, the results were $T_c = 67.0°C$ and $x_c = 33.90$ by weight of phenol.

The critical density ρ_c for the binary liquid mixture phenol – water is found to be 0.8952 g/cm^3 at the critical temperature and concentration.

The specific heat at constant pressure c_p of the binary liquid mixture phenol – water has been measured; the critical c_{pc} and back ground c_{pb} amplitudes of the specific heat at constant pressure have been calculated to be 78.11J/kg.K and 85.29J/kg.K respectively.

The pressure derivative of the critical temperature along the critical line T_c' is calculated for the binary mixture phenol – water to be 9.722×10^{-6} K/Pa.

The critical temperature and critical concentration for the binary liquid mixture phenol – cyclohexane have been measured, the results were $T_c = 17.0°C$ and $x_c = 2.70\%$ by weight of phenol.

The critical density ρ_c for the binary liquid mixture phenol – cyclohexane is found to be 0.7627 g/cm^3 at the critical temperature and concentration.

The pressure derivative of the critical temperature along the critical line T_c' is calculated for the binary mixture phenol – cyclohexane to be 2.8572×10^{-8}K/Pa.

The isobaric thermal expansion coefficient α_p for phenol – cyclohexane binary mixture are calculated at different temperatures, the critical α_{pc} and back ground α_{pb} amplitudes is determined to be 8×10^{-6} K^{-1}, 6×10^{-4} K^{-1} respectively.

The universal quantity R^+_ξ has been calculated from the Two – Scale – Factor Universality realtion   for   phenol – water and   phenol – cyclohexane binary mixtures to be 0.2716 $\pm$0.0005 and 0.2699 $\pm$0.0001 respectively, which indicates that the two mixtures belong to the same class of universality "Two – Scale – Factor Universality"

The measured and calculated parameters for phenol – water binary mixture are summarized in Table (5.1).

Table (5.1) Summary of the measured and calculated results in this work and   previous works for phenol – water binary mixture.

Parameter	This work	Previous works
T_c	67.0°C	66.4°C [a] 69.0°C [b]
x_c	33.90%	34.6% [a] 34.0% [b]
ρ_c	0.8952g/cm^3	-
c_{pc}	78.117 $\frac{J}{kg.K}$	-
c_{pb}	85.292 $\frac{J}{kg.K}$	-
T'_c	9.722 $\times10^{-6}$ K/Pascal	-
R^+_ξ	0.2716	-

[a]:(Howell, 1932),   [b]:(Krishnan, 1935)

The measured and calculated parameters for phenol – cyclohexane binary mixture are summarized in Table (5.2).

Table (5.2) Summary of the measured and calculated results in this work for phenol – cyclohexane binary mixture

Parameter	This work	Previous work
T_c	17.0°C	-
x_c	2.70%	-
ρ_c	0.7627g/cm^3	-
α_{pc}	8×10^{-6} K^{-1}	
α_{pb}	6×10^{-4} K^{-1}	
T_c'	2.8572×10^{-8} K/Pa	-
R^+_ξ	0.2699	-

References

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Appendix A

Table (A.1) Dynamic viscosity measurements at different temperatures and concentrations (0.00% - 35.00%) for the binary liquid mixture phenol – water.

T (°C)	η(cP) 0.00%	η(cP) 10.17%	η(cP) 20.80%	η(cP) 30.20%	η(cP) 31.80%	η(cP) 32.90%	η(cP) 33.90%	η(cP) 35.00%
50.0	0.5468	0.6440	0.6442	1.8324	1.7585	1.6178	1.7504	2.0086
55.0	0.5039	0.6051	0.6052	1.6645	1.4878	1.4632	1.5379	1.9239
57.0	0.4883	0.5685	0.5693	1.4085	1.4136	1.3514	1.4675	1.7226
58.0	0.4808	0.5586	0.5588	1.3395	1.3162	1.3208	1.4361	1.7219
59.0	0.4735	0.5576	0.5582	1.3063	1.3356	1.2555	1.3190	1.6987
60.0	0.4664	0.5589	0.5597	1.3749	1.3185	1.2562	1.3930	1.7474
61.0	0.4594	0.5377	0.5384	1.2513	1.2916	1.2066	1.3296	1.6053
62.0	0.4526	0.5326	0.5331	1.1362	1.2329	1.1726	1.2357	1.5352
63.0	0.4460	0.5077	0.5088	0.9000	1.1812	1.1133	1.1153	1.4098
64.0	0.4395	0.4317	0.4322	0.9528	1.0102	0.9346	0.9553	1.1992
65.0	0.4332	0.4261	0.4268	0.8559	0.9812	0.8762	1.0708	1.0461
66.0	0.4271	0.4143	0.4152	0.7352	0.9709	0.8884	1.0905	0.9736
67.0	0.4211	0.4063	0.4072	0.6449	0.9409	0.9005	1.1088	0.9704
68.0	0.4152	0.4013	0.4021	0.6640	0.9240	0.8892	0.9913	0.8712
69.0	0.4095	0.3996	0.4000	0.5676	0.8781	0.9033	0.7316	0.8579
70.0	0.4039	0.3693	0.3694	0.5481	0.8475	0.7088	0.7573	0.8145
75.0	0.3777	0.3528	0.3531	0.5053	0.7204	0.5893	0.6810	0.7088

Table (A.2) Dynamic viscosity measurements at different temperatures and concentrations (37.10% - 100.00%) for the binary liquid mixture phenol – water.

T (°C)	η(cP) 37.10%	η(cP) 40.20%	η(cP) 49.80%	η(cP) 59.79%	η(cP) 70.40%	η(cP) 79.77%	η(cP) 89.90%	η(cP) 100.00%
50.0	1.9488	1.5864	1.7244	2.3590	2.0292	2.2114	2.0378	3.2917
55.0	1.7383	1.4186	1.5684	1.9790	1.8765	2.1049	1.9385	2.9343
57.0	1.7572	1.3400	1.4636	1.8961	1.8638	2.0251	1.8598	2.6810
58.0	1.6803	1.2906	1.4866	1.8124	1.7483	2.0022	1.8207	2.7050
59.0	1.5926	1.2495	1.4213	1.7759	1.7365	1.9098	1.8151	2.7353
60.0	1.5360	1.2835	1.3437	1.7034	1.7200	1.8575	1.8121	2.5379
61.0	1.4073	1.1500	1.2683	1.6410	1.7206	1.9090	1.8018	2.4598
62.0	1.5408	1.1562	1.2413	1.5885	1.6366	1.7812	1.7689	2.4213
63.0	1.3863	1.0375	1.1741	1.4988	1.6119	1.5964	1.6499	2.2884
64.0	1.2538	0.8750	0.9836	1.2940	1.2438	1.3805	1.3573	2.1701
65.0	1.1637	0.9482	0.9808	1.2448	1.1660	1.2129	1.3432	1.8495
66.0	1.2285	0.9088	0.9318	1.2159	1.1425	1.2034	1.1492	1.8220
67.0	1.1414	0.8510	0.9062	1.2012	1.1209	1.1720	1.1232	1.7905
68.0	1.0755	0.8346	0.8958	1.1601	1.1160	1.1637	1.0880	1.7197
69.0	1.1045	0.8439	0.8566	1.1776	1.1036	1.1680	1.0742	1.6938
70.0	1.0001	0.8297	0.8040	1.0901	1.0003	1.0525	1.0187	1.7790
75.0	0.8853	0.7505	0.7148	1.0120	0.8888	0.9257	0.9464	1.6048

Table (A.3) Dynamic viscosity measurements at different temperatures and concentrations (0.00% - 16.00%) for the binary liquid mixture phenol – cyclohexane.

T (℃)	η(cP) 0.00%	η(cP) 2.00%	η(cP) 2.70%	η(cP) 3.40%	η(cP) 6.70%	η(cP) 9.90%	η(cP) 13.20%	η(cP) 16.00%
14.0	1.0346	0.9721	0.9850	1.0108	1.0366	1.0672	1.1177	1.2670
15.0	1.0181	0.9395	0.9775	0.9925	1.0062	1.0573	1.1166	1.2653
16.0	0.9994	0.9299	0.9567	0.9688	0.9929	1.0385	1.0793	1.2712
17.0	0.9864	0.9040	0.9673	0.9542	0.9786	1.0289	1.0816	1.2677
17.5	0.9855	0.8986	0.9416	0.9557	0.9921	1.0285	1.0801	1.2612
18.0	0.9737	0.8878	0.9233	0.9456	0.9789	1.0161	1.0633	1.2435
18.5	0.9710	0.8796	0.9225	0.9386	0.9658	1.0129	1.0553	1.2282
19.0	0.9627	0.8710	0.9047	0.9286	0.9520	1.0043	1.0426	1.2073
19.5	0.9450	0.8532	0.8895	0.9145	0.9443	0.9829	1.0250	1.1850
20.0	0.9460	0.8525	0.8885	0.9141	0.9302	0.9802	1.0218	1.1799
20.5	0.9339	0.8445	0.8784	0.9001	0.9163	0.9665	1.0076	1.1743
21.0	0.9329	0.8391	0.8769	0.8997	0.9173	0.9670	1.0059	1.1624
22.0	0.9268	0.8170	0.8589	0.8831	0.8963	0.9499	0.9832	1.1368
25.0	0.8930	0.7798	0.8158	0.8424	0.8458	0.8979	0.9255	1.0794
30.0	0.8122	0.6881	0.7342	0.7634	0.7630	0.8197	0.8399	0.9435

Table (A.4) Dynamic viscosity measurements at different temperatures and concentrations (17.90 – 39.70%) for the binary liquid mixture phenol – cyclohexane.

T (℃)	η(cP) 17.90%	η(cP) 19.46%	η(cP) 22.50%	η(cP) 25.50%	η(cP) 31.00%	η(cP) 34.19%	η(cP) 37.00%	η(cP) 39.70%
14.0	1.2779	1.3685	1.4299	1.6194	1.7646	1.8601	2.1255	2.1748
15.0	1.2757	1.3589	1.3970	1.5411	1.7294	1.8189	2.0659	2.1210
16.0	1.2694	1.2928	1.3428	1.4886	1.6838	1.7888	1.9652	2.0263
17.0	1.2510	1.2364	1.3237	1.4363	1.6598	1.7639	1.9560	1.9862
17.5	1.2428	1.2347	1.3114	1.4191	1.6457	1.7444	1.9602	1.9687
18.0	1.2014	1.2224	1.2881	1.4182	1.6252	1.7078	1.9513	1.9289
18.5	1.1920	1.2220	1.2777	1.4073	1.5977	1.6773	1.8615	1.9094
19.0	1.1837	1.1936	1.2624	1.3914	1.5751	1.6499	1.8404	1.8731
19.5	1.1673	1.1671	1.2344	1.3624	1.5357	1.6052	1.8547	1.8365
20.0	1.1423	1.1578	1.2227	1.3606	1.5302	1.5909	1.8257	1.8320
20.5	1.1245	1.1445	1.2092	1.3361	1.5027	1.5694	1.7499	1.7866
21.0	1.1214	1.1330	1.1954	1.3327	1.4974	1.5738	1.7954	1.7833
22.0	1.0972	1.1186	1.1830	1.2665	1.4614	1.5115	1.7023	1.7525
25.0	1.0333	1.0676	1.1076	1.1961	1.3586	1.4162	1.6042	1.6126
30.0	0.9238	0.9382	0.9836	1.0612	1.2028	1.2358	1.4703	1.3778

Appendix B

The dynamic shear viscosities of phenol − water are plotted as a function of temperature at different concentrations of phenol in Figs. (B.1) − (B.5).
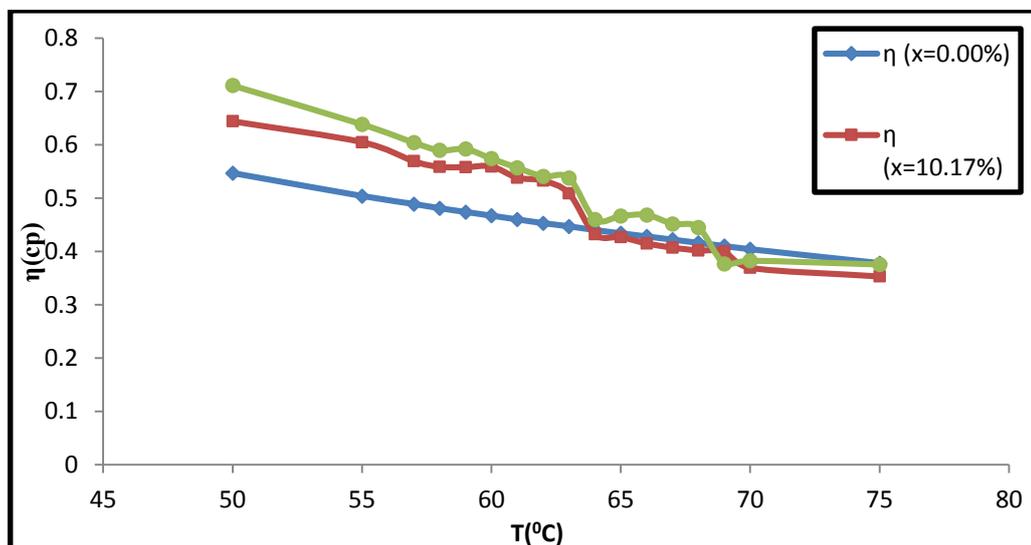

Fig. (B.1) The dynamic shear viscosity of phenol − water mixture as a function of temperature at concentrations 0.00%, 10.17% and 20.80% by weight of phenol.
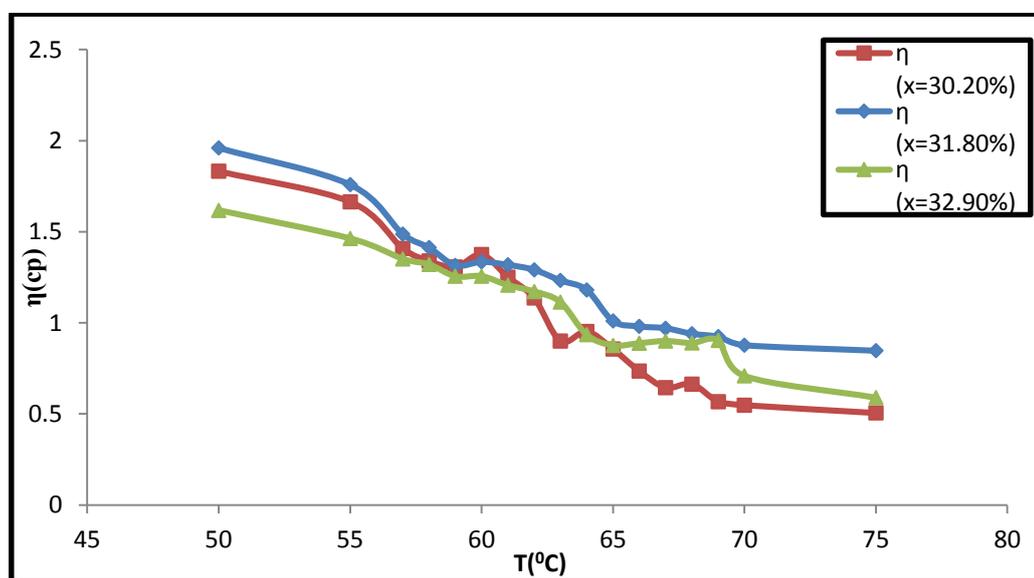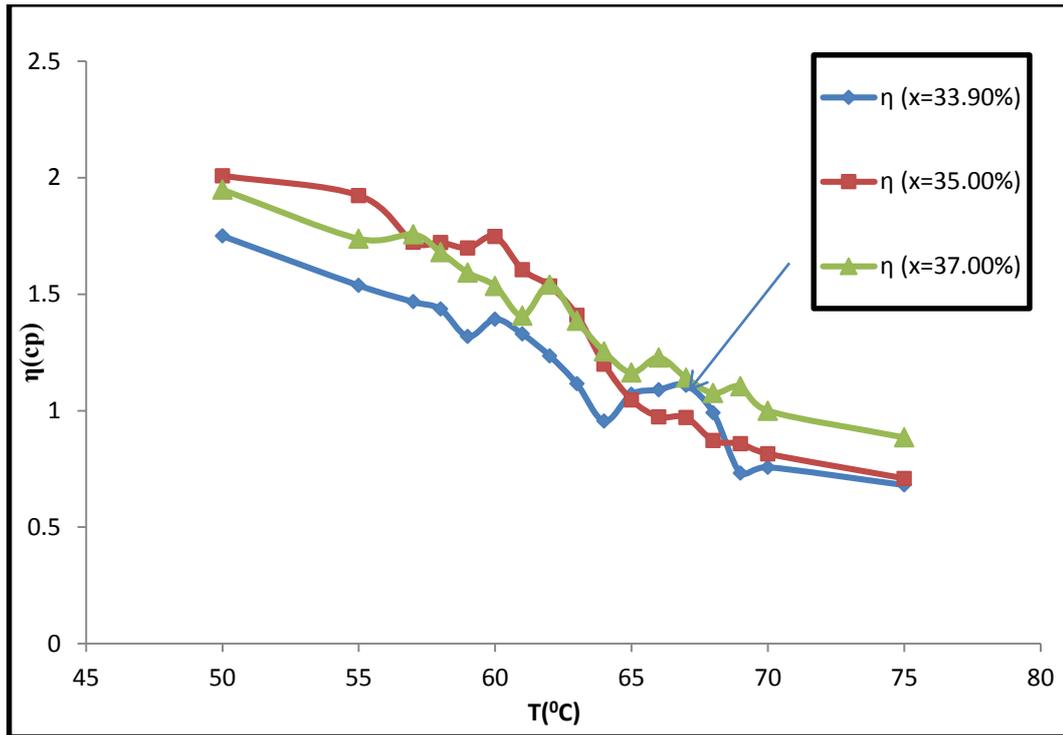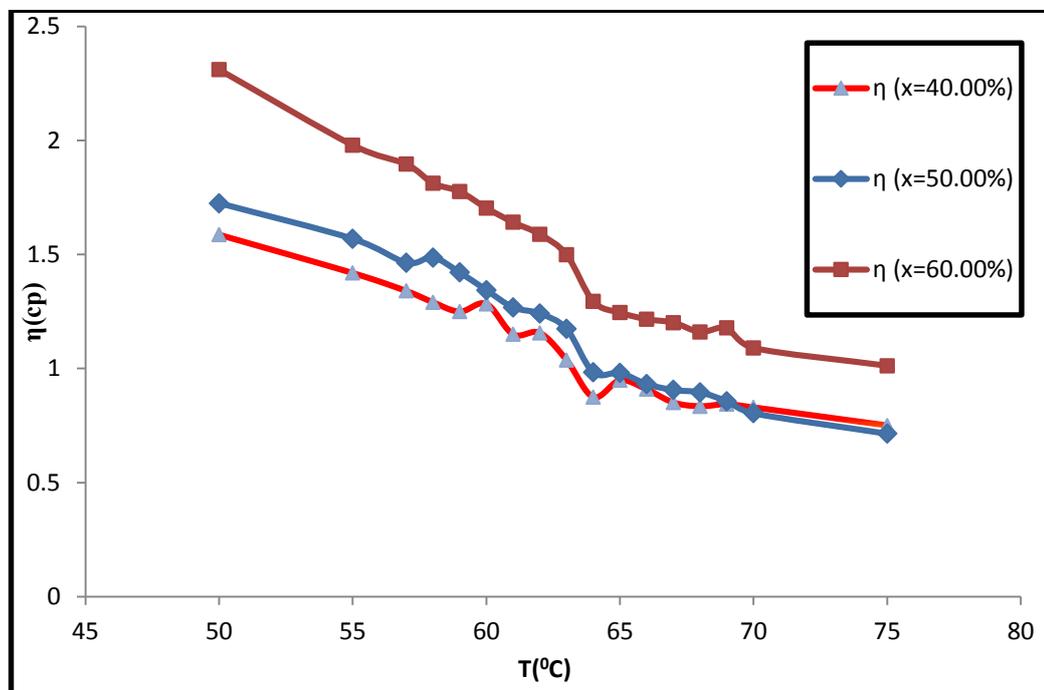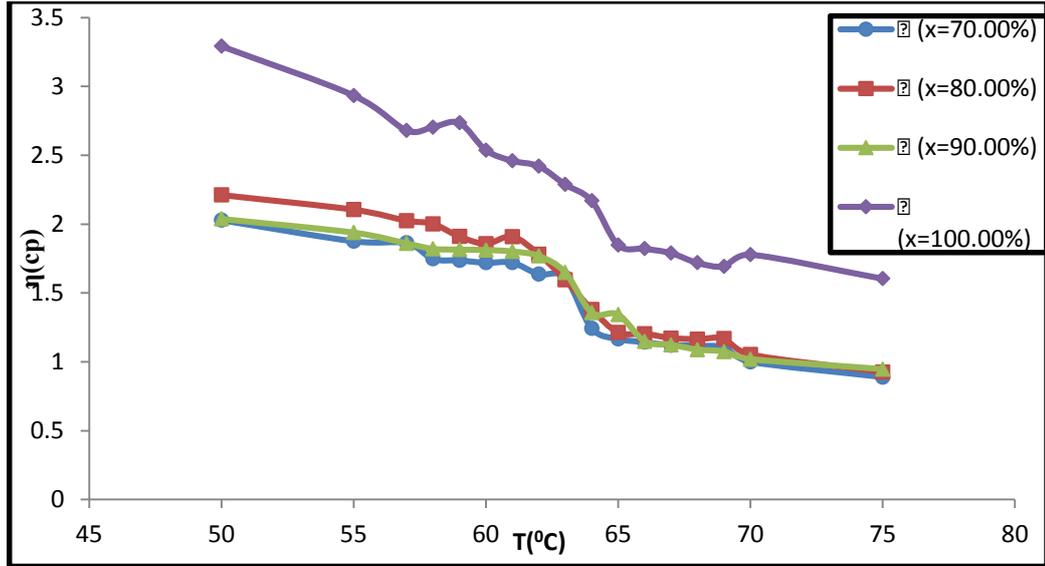

Fig. (B.2) The dynamic shear viscosity of phenol − water mixture as a function of temperature at concentrations 30.20%, 31.80% and 32.90% by weight of phenol.

Fig. (B.3) The dynamic shear viscosity of phenol – water mixture as a function of temperature at concentrations 33.90%, 35.00% and 37.00% by weight of phenol.

Fig. (B.4) The dynamic shear viscosity of phenol – water mixture as a function of temperature at concentrations 40.00%, 50.00% and 60.00% by weight of phenol.

Fig. (B.5) The dynamic shear viscosity of phenol – water mixture as a function of temperature at concentrations 70.00%, 80.00%, 90.00% and 100.00% by weight of phenol.

The dynamic shear viscosities of phenol – cyclohexane are plotted as a function of temperature at different concentrations of phenol in Figs. (B.6) – (B.9).
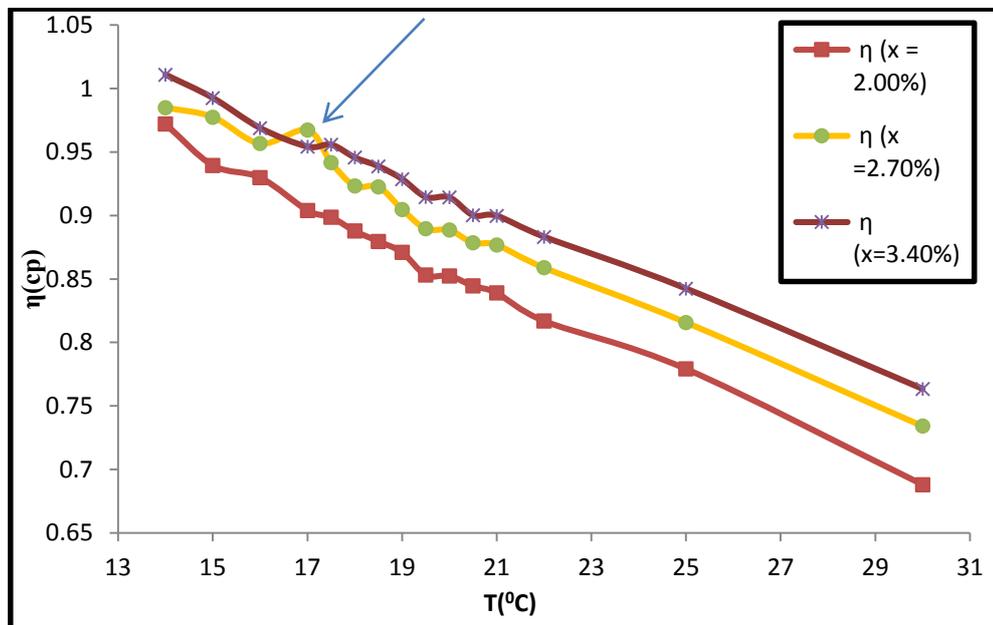

Fig. (B.6) The dynamic shear viscosity of phenol – cyclohexane mixture as a function of temperature at concentrations 2.00%, 2.70% and 3.40% by weight of phenol.
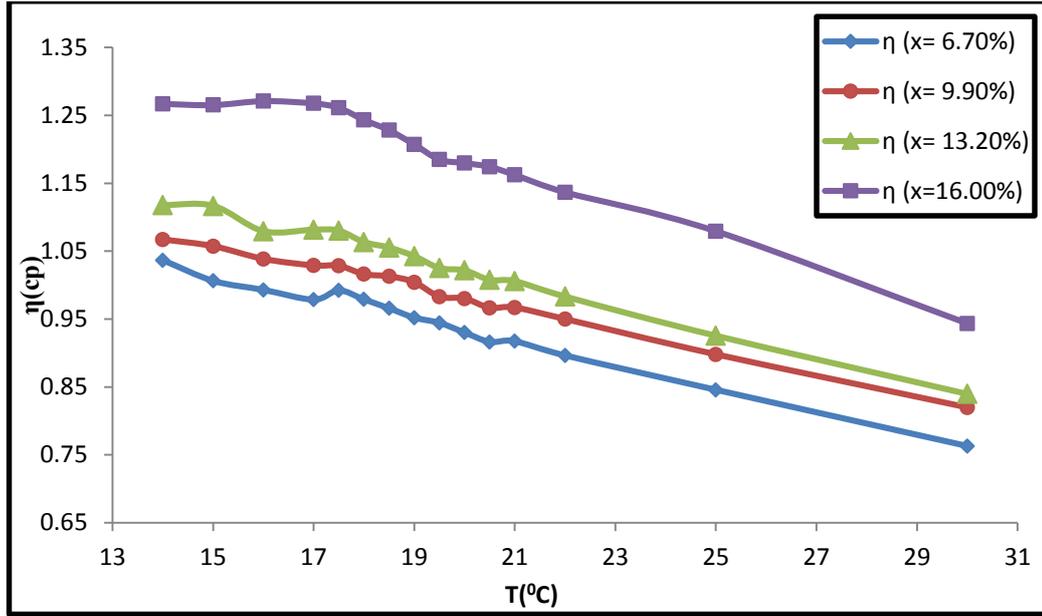
Fig. (B.7) The dynamic shear viscosity of phenol − cyclohexane mixture as a function of temperature at concentrations 6.70%, 9.90%, 13.20% and 16.00% by weight of phenol.
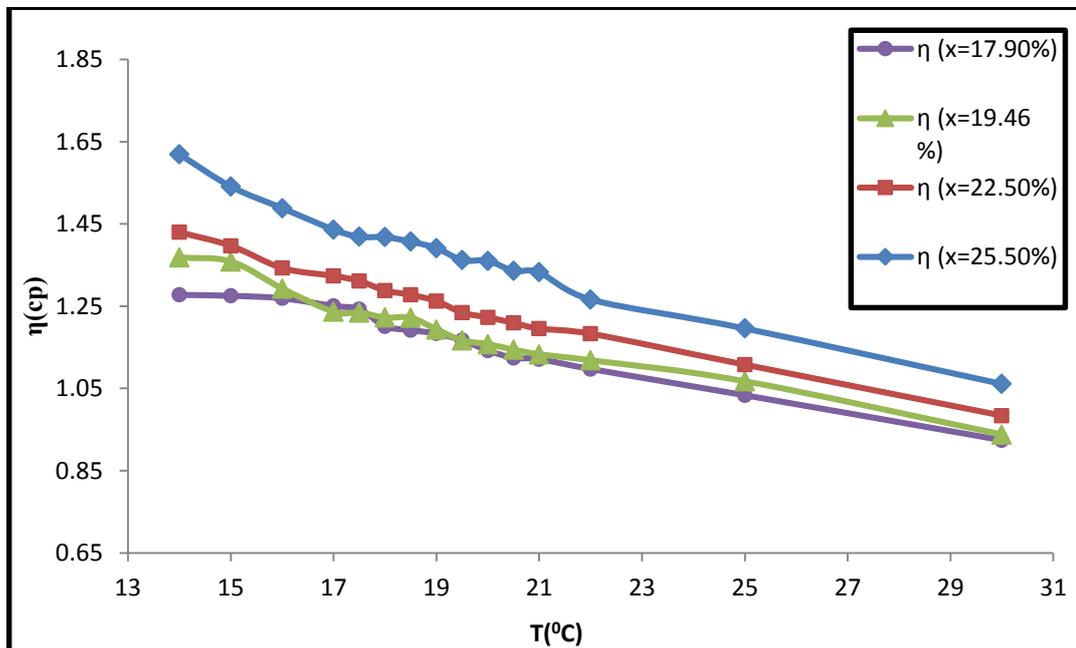

Fig. (B.8) The dynamic shear viscosity of phenol − cyclohexane mixture as a function of temperature at concentrations 17.90%, 19.46%, 22.50% and 25.50% by weight of phenol.
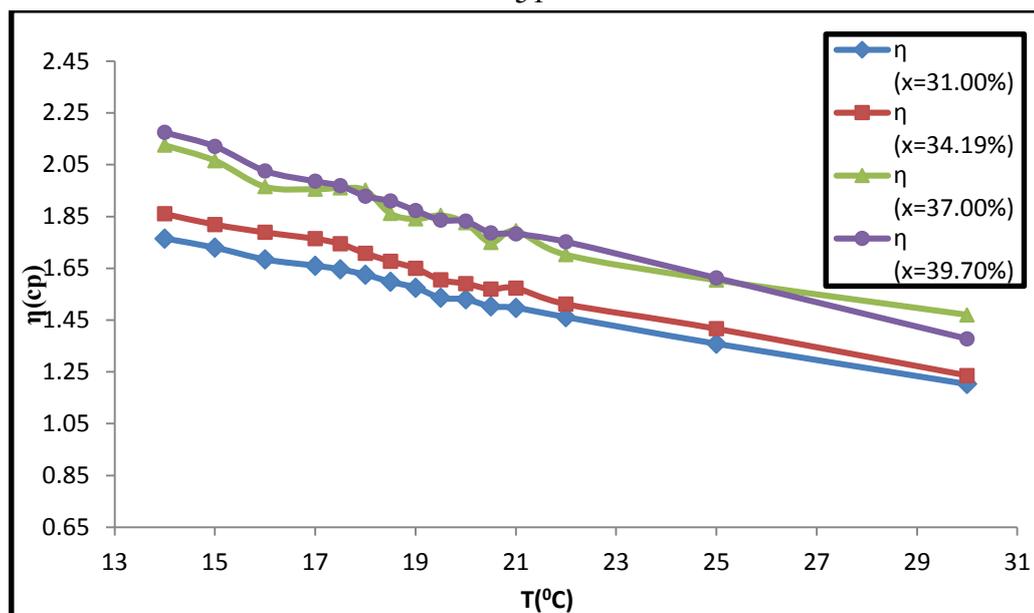
Fig. (B.9) The dynamic shear viscosity of phenol – cyclohexane mixture as a function of temperature at concentrations 31.00%, 34.19%, 37.00% and 39.70% by weight of phenol.

جامعة النجاح الوطنية

كلية الدراسات العليا

المقياس الثنائي العالمي للمخاليط الثنائية الحرجة

إعداد

بلسم نادر عطا

إشراف

أ.د. عصام راشد عبد الرازق

ب

المقياس الثنائي العالمي للمخاليط الثنائية الحرجة
إعداد
بلسم نادر عطا
إشراف
أ.د. عصام راشد عبد الرازق

الملخص

في هذا البحث تم قياس معامل اللزوجة للمخلوط الثنائي الفينول – الماء عند درجات حرارة مختلفة ($50.0°C \leq T \leq 75.0°C$) و تراكيز مختلفة (من 0.00% إلى 100.00%من وزن الفينول), لقد تم تحديد درجة الحرارة الحرجة و التركيز الحرج وكانت النتيجة $67.0°C$ و 33.90% من وزن الفينول على التوالي, تم ايجاد قيمة الكثافة الحرجة عند درجة الحرارة الحرجة والتركيز الحرج للمخلوط الثنائي لتكون $0.8952 g/cm^3$.

تم قياس الحرارة النوعية للمخلوط الثنائي الفينول – الماء للتركيز الحرج عند درجات الحرارة فوق الدرجة الحرجة , تم حساب السعة للحرارية النوعية الحرجة عند ثبوت الضغط لتكون 78.12 = $J/kg.K$.

تم حساب التغيير في درجة الحرارة الحرجة بالنسبة للضغط T_c' لتكون 9.722×10^{-6} K/Pa .

و تم قياس معامل اللزوجة للمخلوط الثنائي الفينول – السايكلوهكسان عند درجات حرارة مختلفة ($14.0°C \leq T \leq 30.0°C$) و تراكيز مختلفة (من 2.00% إلى 39.70% من وزن الفينول). لقد تم تحديد درجة الحرارة الحرجة و التركيز الحرج وكانت النتيجة $17.0°C$ و 2.70% من وزن الفينول على التوالي, تم ايجاد قيمة الكثافة الحرجة ρ_c عند درجة الحرارة الحرجة والتركيز الحرج لتكون $0.7627 g/cm^3$

تم حساب معامل التمدد الحراري الحرج عند ثبات الضغط ليكون 4×10^{-6} K^{-1} .

تم حساب التغيير في درجة الحرارة الحرجة بالنسبة للضغط T_c' لتكون 1.083×10^{-8} K/Pa.

تم حساب قيمة الثابت R^+ء للمخلوط الثنائي الفينول – الماء وكانت النتيجة 0.2716 ± 0.0005

تم حساب قيمة الثابت R^+ء للمخلوط الثنائي الفينول – السايكلوهكسان وكانت النتيجة 0.2699 ± 0.0001 .

القيم المحسوبة للثابت R^+ء تتوافق مع القيمه النظريه والتي تساوي 0.2710 .

ت

مما يدل على ان المخلوطان الثنائيان يندرجان تحت " نظرية المقياس الثنائي العالمي للمخاليط الثنائية الحرجة"