An-Najah National University Faculty of Graduate Studies

Debye Momentum Cutoff of the Critical Binary Mixture of Carbon Tetrachloride and Coconut Oil

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Dedication

For my parents with all love.

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Debye Momentum Cutoff of the Critical Binary Mixture of Carbon Tetrachloride and Coconut Oil

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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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Abstract

The dynamic shear viscosity coefficients of the binary liquid mixture carbon tetrachloride and coconut oil for different temperatures and concentrations are measured using digital viscometer with UL adapter. Shear viscosity anomaly is clearly observed near the critical temperature T_c = 22.2 °C and the critical concentration $x_c = 0.732$ by weight of carbon tetrachloride. Debye parameter L (the intermolecular force range) was calculated using a Light scattering formula to be L = 5.5 Å. Mode Coupling Theory (MCT) of the dynamic shear viscosity is used to fit our experimental data above the critical temperature in the range $0.05 \le T-T_c \le$ 8 °C. It is found that the noncritical part of the dynamic shear viscosity (background viscosity) $\eta_0 = 2.59$ cP and the Debye momentum cutoff (the upper cutoff wave number) $q_D = 0.126 \text{ Å}^{-1}$. The MCT universal constant A is measured to be A = 0.054 which is consistent with the theoretical value. The correlation coefficient (\mathbb{R}^2) value is 0.85, which shows that there is a good fitting.

Chapter One Introduction

1.1 Binary Liquid Mixtures:

A binary liquid mixture is a combination of two pure liquid substances, which have a limited solubility of each one in the other (Popiel; 1964), like carbon tetrachloride-coconut oil, aniline-cyclohexane, and triethylaminewater binary mixtures.

1.1.1 The Critical Point:

The temperature and concentration above which the two liquids become completely miscible at all proportions called critical temperature T_c and critical concentration x_c , respectively. This point; where phase transition occurs, is called the critical point. For a pure liquid the critical point is the end of the vapor-liquid coexistence curve as shown in Figure 1.1.

Many properties for different binary mixtures have been studied near their critical point; like dynamic shear viscosity, bulk viscosity, thermal expansion coefficient, heat capacity, ultrasonic propagation, sound attenuation, ultrasonic velocity (Fixman; 1962), refractive index (Repin *et al*; 1988), and other physical properties.



Figure 1.1: The critical point for (a) a pure and (b) a binary fluid with different types of phase transitions.

1.1.2 Dynamic Theories Near the Critical Point:

There are three main statistical theories that describe the dynamics of the fluid mixtures near the critical point:

I. Mode Coupling Theory (MCT): it 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). These ideas were more fully developed by Kawasaki and Kadanoff and Swift in what is now known as MCT (Kawasaki; 1970, Kadanoff and Swift; 1968). They derived the phenomenological nonlinear Langevin equations of motion from the generalized nonlinear Langevin equations. The basic idea is that nonlinear couplings between the slow dynamical modes (the conserved variables and the order parameter); like concentration or density, can lead to divergences in kinetic coefficients. The nonlinear couplings were of a non-dissipative nature (Gunton; 1979).

- II. Renormalization Group Theory (RGT): it is an advanced statisticalmechanical theory developed originally by Halperin and Hohenberg and Ma (Halperin *et al* ; 1972, Hohenberg and Halperin; 1977). The idea is that there exist a second source of nonlinear couplings between the slow modes (gross variables) which are of a dissipative nature and can cause kinetic coefficients for relaxation models to vanish at the critical point. It has provided a clarification of the nonlinear Langevin equations. These dissipative couplings are important in determining critical exponents and scaling function (Gunton; 1979). RGT 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).
- III. Dynamic Scaling Theory (DST): it is suggested by Ferrell and collaborators (Ferrell *et al* ; 1967) and developed by Halperin and Hohenberg (Hohenberg and Halperin; 1969). It deals with a scaling function that can be determined directly from acoustical

spectrometry; which is a valuable tool for the experimental verification of theoretical critical system models (Anisimov; 1991).

1.2 Literature Review:

Experiments show that certain thermodynamic and transport properties of a binary mixture like shear viscosity, heat capacity and thermal expansion behave anomalously in the vicinity of the critical point.

The first experimental observation that the shear viscosity of a two component system increases dramatically near the solution critical point was in 1959 (Reed and Taylor; 1959).

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).

The theoretical analysis of the shear viscosity for a binary mixture is applied to a model Van der Waals mixture, the result is that it behaves anomalously near the critical point (Deutch and Zwanzig; 1967).

Kawasaki proposed models which are extensions to dynamical domains of Kampen's approach to Van der Waals fluids, and are suited for studying transport phenomena near critical points, the models was used to obtain the lowest order corrections of critical fluctuations to transport coefficients (Kawasaki; 1969).

The anomalous behavior of shear viscosity has been detected experimentally as a function of temperature and for temperature close to the critical one as a function of concentration (Sengers; 1972, Abdelraziq; 1996, 2000, 2001, 2002, 2005, Abdelraziq *et al*; 1990, 1993, 1996).

MCT predicts, for a continuous phase transition, a power and a logarithmic form for the dynamic shear viscosity near the critical point (Kawasaki; 1971, Perl and Ferrell; 1972).

The power law divergence of the kinetic coefficients near the critical point is characterized by critical exponents. There are many types of critical exponents like; viscosity exponent, susceptibility exponent, correlation length exponent and heat capacity exponent. These critical exponents are universal constants and are calculated using RGT and Mean field theory, this universality is proven by experimental data (Dodgson; 2001).

MCT predicts a value of the universal constant A in the theory to be 0.054 (Kawasaki; 1976). The RGT gives a value of A to be 0.053 for the reduced temperature expansion to first order, and 0.065 for the second order, and 0.051 for the third order (Bhattacharjee and Ferrell; 1983).

The correction of the experimental data for the shear viscosity of the binary mixtures near the critical point due to the presence of shear gradients and frequency effects should be considered in order to evaluate the constant A (Nieuwoudt and Sengers; 1989).

Light scattering experiment was used by Debye to study the critical binary mixtures. The correlation length, the intermolecular force range (Debye parameter) and the cutoff coupling wave vector (Debye momentum cutoff) between the mixture molecules was defined extensively. He predicted the divergence of the correlation length as T approaches T_c . An experimental relation between the correlation length and the intermolecular force range also was given (Debye; 1959).

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The general form of the correlation length as a function of temperature and concentration had been calculated using a scaling equation of state (D'Arrigo *et al*; 1977).

The critical amplitude ξ_0 of the correlation length ξ has been experimentally determined for a wide variety of binary mixtures, using various techniques involving light scattering, x-ray scattering, turbidity, calorimetric and viscosimetric measurements (Beysens *et al* ; 1982). The value of the critical amplitude can differ markedly depending on the testing method (Souto-Caride; 2006).

Universality of the binary mixtures and fluids has been investigated, they belong to the same class of universality (Fast and Yun; 1987, Abdelraziq; 2003).

Shear viscosity for ternary liquid mixtures near their critical points has been measured, the viscosity anomaly appears with the same qualitative features as in a binary mixture or in a pure fluid (D'Arrigo *et al* ; 1977).

Quantum mode coupling theory (QMCT) for pure and binary liquids has been developed in order to study super-cooled liquids where quantum fluctuations may compete with thermal fluctuations. The theory was applied to a generic model of a binary mixture of lennard-Jones particles (Rabani and Reichman; 2005).

During the past decade, computer simulation techniques for investigating the nature of the critical behavior of fluids and fluid mixtures have improved considerably. Specifically, it has become possible to obtain accurate information from Monte Carlo (MC) and Molecular Dynamics

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(MD) simulations about the critical mixtures properties, such as the equation of state and the correlation length near critical points (Kim *et al*; 2003).

The ultrasonic propagation of the binary mixture carbon tetrachloride and coconut oil has been measured as a function of temperature near the critical temperature in the low frequency region, a small velocity dispersion was observed in the system (Bhattacharya and Deo; 1983).

The ultrasonic velocity and absorption at the critical concentration were measured as a function of temperature and frequency for the binary mixture CCl_4 -coconut, and the viscosity measurements were made. The coefficient of viscosity of the critical mixture shows a different temperature dependence from that of the pure components (Abdelraziq *et al*; 1992).

1.3 Objectives and Motivations:

Phase transition of the binary mixtures is one of the important subjects nowadays. Measuring the dynamic shear viscosity is one of the methods that are used to study the critical behavior of the binary mixtures.

The binary mixture of CCl_4 and coconut oil is an important mixture, there is no sufficient information about its physical properties; this will be a motivation to measure its viscosity and study the critical behavior of it. In order to do so, the following procedures will be done:

Measuring the dynamic shear viscosity coefficients η for the binary mixture CCl₄-coconut oil over the entire concentration range and over a large range of temperature.

- Fitting the pure components of CCl₄ and coconut oil viscosity data to the pure liquid logarithmic equation.
- Determining the critical point (T_c, x_c) for the mixture CCl₄-coconut oil.
- Applying the MCT approach to determine: the noncritical part of shear viscosity η₀, the universal constant A, the Debye momentum cutoff q_D, and the Debye parameter L for the binary system CCl₄coconut oil.

1.4 Organization of the Thesis:

In chapter 2, the theoretical background of the experimental work will be discussed; such as the theory of viscosity for pure and binary liquids, the binary mixtures light scattering results and the MCT approach. In chapter 3, the methodology of the experiment: measuring, calculations, and fitting of the data will be clarified. The measured data will be given in chapter 4, the critical point will be determined and the viscosity data near the critical point will be analyzed using MCT. A comparison between our results and literatures also is done. In chapter 5, the conclusion of this work and future works will be displayed.

Chapter Tow

Theoretical Background

2.1 Introduction to Viscosity:

Viscosity is one of the main subjects of Rheology; the science that interested in the study of deformation and flow of matter. It is a measure of a fluid (gas or liquid) internal resistance to flow and it refers to the internal friction force between adjacent layers of a fluid, such friction opposes the development of velocity differences within the fluid layers. The opposite of the viscosity is the fluidity which measures the mobility for fluid layers. Viscosity is affected by the temperature and composition of the fluid and, for compressible fluid, also by pressure. Almost all real fluids are viscous, but a fluid which has no resistance to flow known as an ideal fluid which in addition satisfies the following conditions (Serway; 2012):

- Incompressible (density is constant).
- Motion is steady (velocity, density and pressure don't change with time).
- Motion without turbulence (the fluid makes no rotational motion but translational).

To illustrate the concept of viscosity, consider the two horizontal, parallel plates spaced by a distance d, and separated by a liquid as shown in Figure 2.1, assuming that the plates are very large with a large area A, such that edge effects may be ignored. The lower plate is fixed, and the upper is moving to the right with a velocity v under the action of an external force F.



Figure 2.1: Two horizontal, parallel plates spaced by a distance *d*, and separated by a liquid.

The force required to move the upper plate and distort the liquid is proportional to the area A and the speed of the fluid v and inversely proportional to the distance between the plates d. This can be expressed as (Serway; 2012):

$$\frac{F}{A} = \text{shear stress} = \text{shear modulus (S)} \times \text{strain}\left(\frac{\Delta x}{d}\right)$$
$$\frac{F}{A} = S \frac{v \,\Delta t}{d} = S \,\Delta t \,\frac{v}{d}$$
(2.1)

where S is the shear modulus measured in Newton $/m^2$.

At steady state conditions, the velocity between the two plates is linear, then every infinitesimal segment of the line is expressed by the same relation:

$$\frac{F}{A} = -\eta \,\frac{\partial v}{\partial y} \tag{2.2}$$

where η (= S Δt) is the dynamic shear viscosity coefficient with the unit of (Poise = dyne.sec/cm²) and it is usually measured in Centipoise (1cP =

mPa.sec), and $\frac{\partial v}{\partial y}$ is the velocity gradient or shear rate (1/sec); it measures the change in velocity in a direction perpendicular to shear stress.

The negative sign expresses the fact that the shear stress is applied from a region of higher velocity to a lower one.

The kinematic viscosity v is defined as the dynamic shear viscosity divided by the density of the liquid ρ at the same temperature and pressure (Viswanath *et al*; 2007):

$$v = \frac{\eta}{\rho} \tag{2.3}$$

with the unit of (Stokes = 10^{-4} m²/sec), usually measured in Centistokes (1cSt = 10^{-6} m²/sec).

The relation (2.2) is known as Newton's law of viscosity; the shear stress between adjacent fluid layers is proportional to the negative value of the velocity gradient between the two layers. It is a constitutive equation (like Hooke's law, Fick's law, Ohm's law); not a fundamental law of nature but an approximation that holds in some materials and fails in others. Accordingly, fluids are broadly divided into (Viswanath *et al* ; 2007):

- Newtonian: which behaves according to Newton's law of viscositythe viscosity of a liquid remains constant and is independent of the applied shear stress and rate, like water and gases.
- Non-Newtonian: when liquids viscosity depend on the applied shear stress and rate, they are divided into:

- I. Time independent: the relation between the shear rate and stress is not linearly proportional, like psuedoplastic and dilatants liquids.
- II. Time dependent: the fluids display a change in viscosity with time under conditions of constant shear rate (RPM), like Thixotropic and Rheopectic materials.

2.2 Dynamic Shear Viscosity of Pure Liquids:

The viscosity of liquid in general decreases with increasing temperature; the relationship can be expressed in the form of an Arrhenius-type equation (Clements *et al* ; 2006):

$$\eta = \eta_0 \; e^{\frac{E\eta}{RT}} \tag{2.4}$$

where η is the measured dynamic shear viscosity in cP, η_0 is the dynamic shear viscosity at some reference temperature, E_{η} is the temperature coefficient for viscosity, it has the physical significance of activation energy (J/mol), R is the universal gas constant (J/mol.K) and T is the absolute temperature (K).

Equation (2.4) has failed to provide a good representation of real phenomena for all fluids, it indicates the presence of scientific gap for which new equation is needed. The proposed equations are:

I. Two-constant equation: it can be written in an Andrade exponential equation or Duhne logarithmic equation form (Andrade; 1930, Duhne; 1979):

i.
$$\eta = C' e^{B/T}$$
 or $\ln \eta = C + \frac{B}{T}$ (2.5)

II. Three-constant equation: this form of equation is more accurate than the two-constant form (Vogel; 1921):

1.
$$\ln \eta = C - \frac{B}{T+D}$$
 (2.6)

III. Multi-constant equation: Some equations with more than three constants have been proposed to improve upon the accuracy of representation, particularly over wider ranges of temperature, one of them is the polynomial representation (Poling *et al* ; 1987):

$$\operatorname{Ln} \eta = C + \frac{B}{T} + DT + G T^{2}$$
(2.7)

where for the equations (2.5), (2.6) and (2.7), η is the dynamic shear viscosity in cP, T: is the absolute temperature in K and B, C', C, D and G are positive constants and are characteristics of each material.

2.3 Binary Liquid Critical Dynamics:

Far from the critical point of a binary liquid mixture, the behavior of the viscosity is like pure liquids, the situation becomes more complicated around the critical point. To simplify the discussion around the critical point, a binary Van der Waals mixture model will be considered.

2.3.1 Binary Van der Waals Mixture:

Consider a sample of a binary liquid mixture of species O with N₀ particles and species H with N_H particles; the total number of particles N, in a volume V of n cells each of volume ℓ^3 as shown in Figure 2.2. Each cell is large enough to contain many molecules, but still small enough so that the weak long-range interaction varies very slowly within a single cell. The molecules of the two liquids are assumed to be nearly spherical so to interact via a pair-wise potential u(r) which depends only on the mutual distance r between the centers of a two molecules. The potential consist of a short-range hard-core repulsion of range σ , and a long-range attraction (which is the dominant interaction in the theory) with the molecular force range L (Kawasaki; 1969).



Figure 2.2: A cell with a dimension ℓ of a binary liquid mixture of O and H particle types with a coupling wave vector q, illustrates the concentration fluctuation on the length scale $\ell = 2\pi/q$.

If the potential energy between two molecules is - u(r), the intermolecular force range L (Debye parameter) is defined to be (Debye; 1959):

$$< L^{2} > = \frac{\int u(\mathbf{r}) \, \mathbf{r}^{2} \, \mathrm{d}\mathbf{r}}{\int u(\mathbf{r}) \, \mathrm{d}\mathbf{r}}$$
(2.8)

where d**r** is the volume element.

2.3.2 Mode Coupling Approach:

Mode coupling approach is used to illustrate the critical dynamics of the binary Van der Waals mixtures. Some of the concepts in the MCT will be first defined; like: density fluctuations $\rho(r)$, density correlation function C(r), correlation length ξ , structure factor S(q), and coupling wave vector q. The dynamic shear viscosity is then described, according to MCT, in a power and a logarithmic form near the critical point.

2.3.2.I Density Correlation Function:

length r (Reichman and Charbonneau; 2005).

In the mode coupling approach the most important observable is the density (or concentration) fluctuations $\rho(r)$, which fluctuates around the average density ρ_0 in equilibrium as shown in Figure 2.3.

 $\rho(\mathbf{r})$ describes the distribution in a system of N particles with positions r_j , j = 1, 2, ..., N and it is given as (Reichman and Charbonneau; 2005):

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

(2.9)



Figure 2.3: Space evolution of the density fluctuations $\rho(\mathbf{r})$, illustrates the correlation

It is important to know how much a correlation exists between the fluctuations in two points a distance apart. This correlation 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 as shown in Figure 2.3, divided by the average square of the fluctuations (Debye; 1959):

$$C(r) = \frac{\langle \rho(r_0) \rho(r_0 + r) \rangle}{\langle |\rho(r)|^2 \rangle}$$
(2.10)

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 .

The correlation length r (which mustn't be more than the dimension of the cell ℓ) have the symbol ξ in the MCT, it measures the range of concentration (or density) fluctuations in real space. The correlation function can be used to define the correlation length ξ (Debye; 1959):

$$\langle \xi^2 \rangle = \frac{\int C(\mathbf{r}) \, \mathbf{r}^2 \, d\mathbf{r}}{\int C(\mathbf{r}) \, d\mathbf{r}}$$
 (2.11)

It gives the average value of the squared correlation length, because the average value of the correlation length is zero.

2.3.2.II Light Scattering Experiments Results:

Light scattering experiments essentially measure the light scattered intensity from a binary liquid unit cell, this light intensity is called the static structure factor S(q), it is the simplest function characterizing the

equilibrium structure of the cell. The correlation function C(r) can be given from S(q), in fact; each one is a Fourier transform of the other (Reichman and Charbonneau; 2005).

The Fourier transform of the density fluctuations $\rho(\mathbf{r})$ is:

$$\rho(q) = \sum_{j} e^{iqr_{j}} \tag{2.12}$$

The static structure factor S(q) is then written for a binary mixture system of N particles as:

$$S(q) = \frac{\langle |\rho(q)|^2 \rangle}{N}$$
 (2.13)

where the variable q is the coupling wave vector which measures the range of the density fluctuations in reciprocal space. The upper cutoff value for q is equal to $(2\pi / \text{dimension of the cell } \ell)$, and it is called the Debye momentum cutoff with the symbol q_D as shown in Figure 2.2.

The coupling wave vector q is conjugate to the correlation length ξ , far away from the critical temperature the relation $q_D \xi = 1$ is hold (Nieuwoudt and Sengers; 1989).

Light scattering intensity measurements determined the correlation length temperature dependence near the critical point (Chang *et al* ; 1971):

$$\xi = \xi_0 \tau^{-\nu} \tag{2.14}$$

where ξ_0 is the critical amplitude of the correlation length of the concentration fluctuations, $\tau \ (= \frac{(T-T_c)}{T_c})$ is the reduced absolute temperature which measures the distance from the critical temperature T_c and $\nu \ (= 0.64)$ is a critical exponent (D'Arrigo et al; 1977, Klein and Woermann; 1978).

This can be described as follows; in approaching the critical temperature, not only the amplitude of the fluctuations, but also their correlation length increases.

Light scattering experiments also predict that around the critical point, a relation between the correlation length ξ and the intermolecular force range L of the following form should be exist (Debye; 1959):

$$\xi^2 = \frac{L^2}{\tau} \tag{2.15}$$

where τ is the reduced absolute temperature.

Klein and Woermann show that the modified form of equation (2.15) is (Klein and Woermann; 1978):

$$L = 2.45 \xi_0 T_c^{\frac{(v-1)}{2}}$$
(2.16)

where x (= 1.25) is the universal critical exponent of the isothermal compressibility and T_c is the critical temperature for the binary system in K.

The intermolecular force range gives an indication of the molecules diameter so it is an important quantity to be evaluated.

2.3.2.III Shear Viscosity Near the Critical Point:

MCT predicts a divergence of the kinetic coefficients near the critical point, one of the kinetic transport coefficients is the dynamic shear viscosity η . To describe the divergence of η near the critical point, two contributions must be considered: the critical part; which is dominant near the critical point, and the regular part; which is dominant far away from it.

Then, the dynamic shear viscosity η near the critical point can be written as a power law (Kawasaki; 1976):

$$\eta = \eta_0 \tau^{-\nu x_{\eta}} \tag{2.17}$$

where, τ is the reduced absolute temperature, η_0 is the noncritical part of the dynamic shear viscosity in cP, and v x_η is the critical exponent for the viscosity anomaly and it is equal to 0.04 (Klein and Woermann; 1978, Abdelraziq; 2002).

The MCT of Perl and Ferrell predicts the logarithmic temperature dependence of the hydrodynamic viscosity near the critical point (Perl and Ferrell; 1972):

$$\frac{\Delta \eta}{\eta} = \frac{(\eta - \eta_0)}{\eta} = A \ln \left(q_D \xi \right)$$
(2.18)

where η is the dynamic shear viscosity at the critical concentration in cP, η_0 is the background viscosity, A is a MCT universal constant predicted to have the theoretical value $0.054 = \frac{8}{15\pi^2}$ (Kawasaki; 1976), q_D is the upper cutoff wave number (Debye momentum cutoff) in Å⁻¹ and ξ is the correlation length of the concentration fluctuations in Å.

Chapter Three Methodology

The two high purified chemicals of CCl_4 and coconut oil are used to prepare the samples of the binary mixture with different concentrations. The viscosity of the samples is measured using digital viscometer with UL adapter. The experimental results are analyzed statistically using Excel program.

3.1 Carbon Tetrachloride and Coconut Oil:

The two high purified chemicals that will be used in this work are:

- 1. Carbon Tetrachloride CCl_4 : it is an organic compound that exist at room temperature as a colorless, clear, heavy liquid with strong ethereal odor. The symmetrical geometry of CCl_4 make it non-polar, so it dissolves other non-polar compounds like fats and oils (Brezina *et al* ; 1986).
- 2. Coconut Oil: it is an edible oil with delicious odor. It belongs to unique group of vegetable oils called lauric oils, the chemical composition is shown in Table 3.1. There are no closed molecular formula. Coconut oil thermal and oxidative degradation and the analysis of the low-temperature properties have been investigated. Coconut oil shows oxidative stability, this can be attributed to the predominantly saturated nature of its fatty acid constituents (Jayadas and Nair; 2005).

Table 3.1: Chemical composition of coconut oil (Hilditch; 1956, Apple white; 1980, Hui YH; 1996).

Component	Fraction (%)
Lauric acid (CH ₃ (CH ₂) ₁₀ COOH)	51.0
Myristic acid (CH ₃ (CH ₂) ₁₂ COOH)	18.5
Caprilic acid (CH ₃ (CH ₂) ₆ COOH)	9.5
Palmitic acid (CH ₃ (CH ₂) ₁₄ COOH)	7.5
Oleic acid (CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COOH)	5.0
Capric acid (CH ₃ (CH ₂) ₈ COOH)	4.5
Stearic acid (CH ₃ (CH ₂) ₁₆ COOH)	3.0
Linoleic acid	1.0
(CH ₃ (CH ₂) ₄ CH=CHCH ₂ CH=CH(CH ₂) ₇ COOH)	1.0

Some physical and chemical properties for the two substances are given in

Table 3.2.

Table 3.2: Some physical and chemical properties of CCl₄ and coconut oil chemicals (HSDB; 2009, Burkle GmbH; 2011, MSDS; 1989).

Compound	Color	T _{boiling} °C	T _{melting} °C	ρ(20°C) Kg/m ³	η (20°C) mPa.sec	Newtonian Or non
CCl ₄	Colorless	77	-23	1594	0.967	Newtonian
Coconut Oil	White to yellowish	>177	21 - 25	920	60	Newtonian

3.2 Samples Preparation:

3.2.1 Density Measurements:

The density of the two pure liquids of CCl_4 and coconut oil is needed to determine the ratio of the mass concentration of the binary mixture. The instruments that were used to measure the density are:

- HX-Z Electronic Balance: it is used to measure the mass of the liquid with accuracy ±0.1 %, it is shown in Figure 3.1.a.
- The 10 ml Pycnometer: it is used to keep a constant volume of the measured sample, it is shown in Figure 3.1.b. It is usually made of

glass, with a close-fitting ground glass stopper with a capillary tube through it, so that air bubbles may escape from the apparatus.



Figure 3.1: (a) Electronic Balance and (b) a Pycnometer used to measure the density. The density ρ is given by:

$$\rho (gm/cm^3) = \frac{mass of the liquid}{10 ml}$$
(3.1)

Binary mixture samples with different concentration should be prepared at the same temperature the density is measured, because the density is affected by the temperature.

The measured average densities for the two substances at room temperature of 25 °C is $\rho_{CCl4} = 1.59 \text{ gm/cm}^3$ and $\rho_{coco} = 0.92 \text{ gm/cm}^3$.

3.2.2 Concentration Measurements:

The mass concentration of carbon tetrachloride x_{CCl4} for a sample consists of CCl_4 and coconut oil in a volume V is given by:

$$x_{CC14} = \frac{mass of CC14}{total mass of the sample} = \frac{(\rho V)_{CC1_4}}{(\rho V)_{CC1_4} + (\rho V)_{coco}}$$
(3.2)

The mass concentration of carbon tetrachloride is 77.6 % for a binary mixture consists of 20 ml of CCl_4 and 10 ml of coconut oil at 25°C.

3.3 Experimental apparatus:

3.3.1 Viscosity apparatus:

A Brookfield Viscometer Model DV-I+ with UL adapter is used to measure the dynamic shear viscosity as shown in Figure 3.2.a. It consists of a set of seven spindles (RV SPINDLE SET) with accuracy $\pm 1\%$. The spindles measure viscosity range from 0.01 up to 13300000 cP. The rotational speed of the spindles are two set. The first is: 0.0, 0.3, 0.6, 1.5, 3, 6, 12, 30, 60 RPM and the second set is: 0.0, 0.5, 1, 2, 2.5, 4, 5, 10, 20, 50, 100 RPM.

The principle of operation is to drive a spindle (which is immersed in the test fluid) through a calibrated spring. The viscous drag of the fluid against the spindle is measured by the spring deflection. Spring deflection is measured with a rotary transducer. The viscosity range of a DV- I + viscometer (in cP) is determined by the rotational speed of the spindle, the size and shape of the spindle, the container the spindle is rotating in, and the full scale torque of the calibrated spring (Brookfield manual; 1999).



Figure 3.2: (a) A Brookfield Viscometer Model DV-I+ with UL adapter connected to the refrigerated and heating circulator and (b) the accessories of the UL adapter.

UL adapter:

The Brookfield UL adapter accessory is shown in Figure 3.2.b. It is used to make accurate and reproducible measurements with low viscosity, for Newtonian and non-Newtonian materials. It is usually operated with spindle number 0 at 60 RPM. It consists of a precision cylindrical spindle rotating inside a machined tube. The tube has a removable end cap and thus can be used in a beaker or tank when open. With the cap in place, the closed tube holds 30 ml of the sample. A water jacket is provided to control the temperature of the sample cell, with inlet and outlet attached with a thermostatic device consisting of a constant temperature water bath and a water-pump circulating system (Brookfield; 1999).

3.3.2 Temperature Controller:

Julabo F25-MV Refrigerated and Heating Circulator (Figure 3.3.a) with accuracy ± 1 % is used to control the temperature of the sample in the UL adapter (Julabo; 2003).

In addition to Julabo F25-MV, Digital Prima Long Thermometer (Figure 3.3.b) with accuracy $\pm 1\%$ is used to measure the temperature of the sample.



Figure 3.3: (a) Julabo F25-MV Refrigerated and Heating Circulator and (b) Digital Prima Long Thermometer.

3.4 Statistical Analysis:

The measured data were fitted statistically using Excel program. 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. Error bars are also plotted on the curves.

Chapter Four

Results and Discussion

The dynamic shear viscosity η is measured for the binary liquid mixture CCl_4 and coconut oil at different temperatures and concentrations.

The pure liquids ($x_{CCl4}=0$ and $x_{CCl4}=1$) viscosity data is fitted to the logarithmic two-constant equation.

Shear viscosity (kinematics and dynamics) anomaly is detected as a function of temperature and concentration near the critical point (T_c , x_c).

MCT for the dynamic shear viscosity is used to fit the data near the critical point. The power law of the dynamic shear viscosity η is used to determine the background viscosity η_0 , and the logarithmic form of η is used to determine the MCT constant A and the upper cutoff wave number (Debye momentum cutoff) q_D .

The light scattering experiments relation between the correlation length and the intermolecular force range is used to determine L (Debye parameter).

4.1 Dynamic Shear Viscosity Results:

The results of the dynamic shear viscosity η as a function of temperature for different concentrations of carbon tetrachloride are given in Table 4.1.

X _{CCl4}	1	0.9	0.777	0.74	0.732	0.723	0.7	0.6	0.5	0.3	0
T(°C)		η (cP)									
20.00	1.07	1.69	2.37	2.94	3.20	3.31	3.80	7.10	11.50	23.40	56.00
21.00	1.06	1.66	2.30	2.88	3.14	3.20	3.73	7.00	11.10	22.50	55.00
21.50	1.05	1.61	2.24	2.84	3.10	3.10	3.69	6.83	10.90	22.20	54.00
22.25	1.03	1.57	2.20	2.77	3.15	3.04	3.63	6.61	10.60	21.40	52.00
23.00	1.02	1.54	2.18	2.70	2.94	2.97	3.52	6.55	10.20	20.90	51.50
24.00	1.00	1.50	2.16	2.65	2.84	2.93	3.41	6.45	9.71	20.30	48.00
25.00	0.99	1.49	2.13	2.56	2.77	2.85	3.31	6.35	9.45	19.30	46.00
27.00	0.97	1.39	2.03	2.45	2.58	2.64	3.09	6.00	8.70	17.10	40.60
30.00	0.96	1.28	1.81	2.10	2.40	2.45	2.80	5.23	7.85	15.80	32.70
35.00	0.91	1.17	1.60	1.92	2.05	2.08	2.45	4.83	6.72	12.90	25.30
40.00	0.85	1.07	1.30	1.65	1.76	1.86	2.24	4.37	6.08	11.00	19.00

 Table 4.1: The measured dynamic shear viscosity values as a function
 of temperature for different concentrations of carbon tetrachloride.

Table 4.1 shows that at each concentration of carbon tetrachloride, the viscosity decreases as the temperature increases, because when heat is applied to liquids, the molecules can then slide over each other more easily making the liquid to become less viscous. And for each temperature, the viscosity increases as the concentration of carbon tetrachloride x_{ccl4} decreases from 1 to 0, because coconut oil substance is more viscous than carbon tetrachloride.

4.1.1 Viscosity of Pure Components:

The dynamic shear viscosities of the concentrations ($x_{CCI4} = 0, 1$) is given in Table 4.2. The logarithm of the dynamic shear viscosity for these concentrations and the inverse absolute temperatures are calculated.

Table 4.2: The reciprocal of the absolute temperature and the logarithm of the dynamic shear viscosity of the system at the concentration extremes.

T (K)	$\frac{1}{T}$ (K ⁻¹) * 10 ⁻³	$\eta_{(xccl4=0)}(cP)$	$Log\eta_{(0)}$	$\eta_{(xccl4 = 1)}(cP)$	$Log\eta_{(1)}$
293.15	3.41	56.00	1.74819	1.07	0.02940
294.15	3.40	55.00	1.74036	1.06	0.02530
294.65	3.39	54.00	1.73239	1.05	0.02119
295.40	3.38	52.00	1.71600	1.03	0.01284
296.15	3.37	51.50	1.71180	1.02	0.00860
297.15	3.36	48.00	1.68124	1.00	0.00000
298.15	3.35	46.00	1.66276	0.99	-0.00440
300.15	3.33	40.60	1.60853	0.97	-0.01320
303.15	3.29	32.70	1.51455	0.96	-0.01800
308.15	3.24	25.30	1.40312	0.91	-0.04100
313.15	3.19	19.00	1.27875	0.85	-0.07060

The logarithm of the dynamic viscosity for the concentrations ($x_{CCl4} = 0, 1$) is plotted versus the reciprocal of the absolute temperature in Figure 4.1.



Figure 4.1: The logarithm of the dynamic shear viscosity versus the reciprocal of the absolute temperature for $x_{CCl4} = 0, 1$.

Figure 4.1 shows a linear relation between log η and T⁻¹ for the pure components with the equations:

$$\log \eta = \frac{2235.2}{T} - 5.8506$$
 for coconut oil (4.1)

and

$$\log \eta = \frac{431.62}{T} - 1.4467 \quad \text{for CCl}_4 \tag{4.2}$$

The pure components viscosity equations can be fitted to Equation 2.5: (Log $\eta = \frac{B}{T} + C$). The value of C gives the logarithm of the shear viscosity of the given liquid when T approaches infinity.

Table 4.3 shows our values of B and C for CCl₄ and coconut oil compared with the literature values, they are in good agreement with each other.

Table 4.3: The values of the constants B and C for the two pure liquids CCl₄ and coconut oil from literatures and from this work.

	Litera	This work		
Constant	CCl ₄ (Dutt and	Coconut oil	CCI	Coconut oil
	Prasad; 2004)	(Mesquita et al; 2012)	CCI_4	Coconut on
В	541.88	1908.19	431.62	2235.20
С	-1.86	-5.17	-1.45	-5.85

4.1.2 Shear Viscosity Anomaly Near the Critical Point:

The critical point of the binary mixture CCl_4 and coconut oil was determined by Battacharya and Deo . The critical temperature T_c is 22.2 °C and the critical concentration x_c is 0.732 by weight of carbon tetrachloride (Battacharya and Deo; 1983).

The viscosity values in Table 4.1are plotted as a function of concentration of CCl₄ for different temperatures in Figure 4.2.



Figure 4.2: The measured values of shear viscosity versus concentration of carbon tetrachloride for different temperatures.

The dynamic shear viscosity behaves anomalously near the concentration 0.732 by weight of carbon tetrachloride and the temperature 22.20 °C, this gives an indication that this is the critical point ($T_c = 22.20$, $x_c = 0.732$ by weight of CCl₄) for the binary mixture CCl₄ and coconut oil, which is in good agreement with the literature value (Battacharya and Deo; 1983).

The anomalous behavior starts from temperatures nearly 8 °C above the critical temperature $T_c = 22.20$ °C and 2 °C below it, and the amplitude of the viscosity anomaly increases as the temperature approaches the critical temperature.

Dynamic shear viscosity values in Table 4.1 are plotted as a function of temperature for different concentrations of CCl_4 in Figure 4.3.



Figure 4.3: The measured dynamic shear viscosity as a function of temperature for different concentrations of carbon tetrachloride.

Figure 4.3 shows the anomalous behavior of the dynamic shear viscosity at the critical concentration $x_{CC14} = 0.732$, near the critical temperature $T_c = 22.20$ °C. The temperature dependence of the viscosity at the critical concentration is different from that of the pure components; there are no anomalous behavior for pure components.

4.1.3 Kinematic Viscosity Anomalous Behavior:

The kinematic viscosity ν (cSt) at the critical concentration of the binary mixture is calculated for different temperatures in Table 4.4.

The behavior of the kinematic and the dynamic shear viscosity at the critical concentration $x_{CCl4} = 0.732$ near the critical temperature 22.20 °C is shown in Figure 4.4.

Table 4.4: The measured dynamic shear viscosity and density values at the critical concentration are used to determine the kinematic viscosity behavior near the critical temperature.

(°C)	η _c (cP)	ρ (gm/ml)	v _c (cSt)
20.00	3.20	1.217	2.63
21.00	3.14	1.214	2.59
21.50	3.10	1.213	2.56
22.25	3.15	1.207	2.61
23.00	2.94	1.203	2.44
24.00	2.84	1.200	2.37



Figure 4.4: The anomalous behavior of the dynamic and the kinematic shear viscosity at the critical concentration near the critical temperature.

Kinematic shear viscosity shows anomalous behavior near the critical point with the value 2.61 cSt at the critical point, a value that is lower than the dynamic shear viscosity value at that point which is equal to 3.15 cP.

4.2 Application of the Mode Coupling Theory Approach:

The MCT of dynamic shear viscosity of Perl and Ferrell and Kawasaki is applied at the critical concentration slightly above the critical temperature in order to determine the background viscosity η_0 , the MCT constant A and the upper cutoff wave number q_D .

4.2.1 The Background Viscosity η₀:

The data of dynamic shear viscosity coefficients η at the critical concentration above the critical temperature $0.05 \le T - T_c \le 8$ °C are given in

Table 4.5 and the value of $\tau^{-0.04}$ for each viscosity value is also calculated. **Table 4.5: The measured values of dynamic shear viscosity at the critical concentration slightly above the critical temperature and the value of** $\tau^{-0.04}$.

(°C)	T (K)	τ	$ au^{-0.04}$	η (cP)
22.25	295.40	0.0002	1.42	3.15
23.00	296.15	0.0027	1.27	2.94
24.00	297.15	0.0061	1.23	2.84
25.00	298.15	0.0095	1.20	2.77
27.00	300.15	0.0163	1.18	2.58
30.00	303.15	0.0264	1.16	2.40

The measured dynamic shear viscosity η at the critical concentration is plotted versus $\tau^{-0.04}$ as shown in Figure 4.5.



Figure 4.5: The measured dynamic shear viscosity at the critical concentration near the critical temperature versus $\tau^{-0.04}$.

It gives a linear relation which can be compared to Equation 2.17: ($\eta = \eta_0 \tau^{-10.04}$) to observe that the slope is equal to the background viscosity η_0 . A least square fit gives the best value for η_0 , which is equal to 2.59 cP.

Our value of η_0 is in good agreement with the literature value which is equal to 2.59 cP (Abdelraziq *et al*; 1992).

4.2.2 The MCT Constant A:

The MCT of the critical dynamic shear viscosity of Perl and Ferrell and Kawasaki predicts a constant A of the theory with the theoretical value $\frac{8}{15\pi^2} = 0.054$. The value of A can be determined by using Perl and Ferrell logarithmically diverging viscosity law near the critical point which can be written as:

$$\frac{\Delta \eta}{\eta} = \frac{(\eta - \eta_0)}{\eta} = A \ln q_D + A \ln \xi$$
(4.3)

where $\frac{\Delta \eta}{\eta}$ is the relative anomalous dynamic shear viscosity, η_0 is the background viscosity calculated in section (4.2.1) to be 2.59 cP, q_D is the binary mixture upper cutoff wave number; will be determined in the next section, and ξ is the average correlation length of the concentration fluctuations which is given by Equation 2.14: ($\xi = \xi_0 \tau^{-0.64}$); where ξ_0 is the critical amplitude for the correlation length which is a characteristic of each binary mixture.

For our system of CCl₄ and coconut oil, the value of ξ_0 was calculated by Abdelraziq *et al* to be 1.1 Å (Abdelraziq *et al* ; 1992), and it will be used to determine the values of ξ at the critical concentration slightly above the critical temperature. The relative anomalous shear viscosity $\frac{\Delta \eta}{\eta}$ and the logarithm of the average correlation length ln ξ is calculated in Table 4.6 at the critical concentration and above the critical temperature.

Table 4.6: The anomalous shear viscosities at the critical concentration and the logarithm of the average correlation length.

(°C)	T (K)	τ	$ au^{-0.64}$	ξ	Ln ξ	η	∆η/η
22.25	295.40	0.0002	259.20	285.10	5.65	3.15	0.18
23.00	296.15	0.0027	43.96	48.35	3.88	2.94	0.12
24.00	297.15	0.0061	26.16	28.78	3.36	2.84	0.09
25.00	298.15	0.0095	19.72	21.69	3.08	2.77	0.06
27.00	300.15	0.0163	13.96	15.36	2.73	2.58	0.00

The behavior of the average correlation length ξ as a function of the reduced temperature τ is clearly observed in Table 4.6; as $T \rightarrow T_c$ the average correlation length becomes larger and larger, when the temperature reaches the critical temperature the correlation length diverges.

The relative anomalous shear viscosity $\frac{\Delta \eta}{\eta}$ is plotted versus the logarithm of the average correlation length ln ξ in Figure 4.6.



Figure 4.6: The relative anomalous shear viscosity $\frac{\Delta \eta}{\eta}$ versus the logarithm of the average correlation length ln ξ .

Figure 4.6 shows that the relation between $\frac{\Delta \eta}{n}$ and $\ln \xi$ is a linear relation with the slope equals to A value which is 0.0538.

The measured and calculated values of the constant A for different binary mixtures are given in Table 4.7.

The measured value of A in our work is in good agreement with the literature values, and it is independent of the type of the binary mixture.

Table 4.7: The measured and calculated values of A for different

omai y mixtui es.			
Binary system	Calculated A	Measured A	Reference
Aniline-	0.054	0.056	(D'Arrigo et al ; 1977)
cyclonexalle			
Triethylamine-		0.054	(Swinny and Henry;
water		0.034	1973)
CCl ₄ -coconut oil		0.0538	This work

hinary mixtures

4.2.3 Debye Momentum Cutoff q_D:

The upper cutoff wave number q_D , which is a free parameter in MCT, can be found from the intercept of Figure 4.6 and the value of the MCT constant A. Using of Equation 2.18 the value of q_D is 0.126 Å⁻¹. Determining q_D of the binary mixture CCl_4 and coconut oil supports the MCT of the critical viscosity.

4.3 Debye Parameter L:

The intermolecular force range or Debye parameter L can be calculated from light scattering results. A relation between the correlation length and the intermolecular force range is given in Equation 2.16: (L = 2.45 ξ_0 $T_c^{\frac{(s-1)}{2}}$; T_c (= 295.35 K) is the critical absolute temperature for the binary

liquid CCl₄-coconut oil and ξ_0 is 1.1 Å for the binary mixture of CCl₄ and coconut oil (Abdelraziq *et al* ; 1992).

Substituting the values of ξ_0 , T_c, and γ in Equation 2.16, the value of Debye parameter L is 5.5 Å.

The long range value of L indicates that the mutual forces between different molecules, in the binary mixture CCl_4 and coconut oil, can be considered as a weak attractive force.

Chapter Five

Conclusion and future work

Dynamic shear viscosity behaves anomalously near the critical point, the anomalous behavior is explained theoretically using the MCT.

The values of the background viscosity η_0 , the Debye momentum cutoff q_D , and the Debye parameter L were determined for the binary mixture CCl₄ and coconut oil, they are fluid dependent constants. The MCT constant A which is fluid independent, was evaluated, its value is consistent with the theoretical value.

Shear viscosity coefficients and other information about the binary mixtures are important for the scientists working on the improvement of molecular theories.

It is left as a future work to prove the anomalous behavior of other kinetic coefficients near the critical point like; thermal expansion coefficient, heat capacity, refractive index and susceptibility for the binary mixture CCl_4 and coconut oil and for other binary mixtures.

Binary mixtures of different types can be studied experimentally and their measured dynamic shear viscosities can be used to evaluate η_0 , q_D , L and A for the given binary system.

Light scattering measurements can be performed on the binary mixtures to determine the critical amplitude ξ_0 and the critical exponent v that characterize the correlation length ξ of the concentration fluctuations.

Other statistical theories; like RGT and DST, can be used to explain the dynamic shear viscosity results near the critical point for the binary liquid mixtures.

It is left as a future work to use computer simulations to study the molecular properties of the binary mixtures. The two popular types of computer simulations are Monte Carlo (MC) and Molecular Dynamics (MD) numerical techniques.

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جامعة النجاح الوطنية كلية الدراسات العليا

قطع زخم ديباي للخليط الثنائي الحرج رباعي كلوريد الكربون وزيت جوز الهند

إعداد يسر هشام مصطفى كتانة

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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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الملخص