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Faculty of Graduate Studies

Adiabatic Coupling Constant g of the Binary Liquid Mixture Methanol – Cyclohexane

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Dedication

This thesis is dedicated to my parents for their infinite support, as well as to my whole family and friends

With respect and love

This thesis is also dedicated to Miss Diana Dhyliah, Miss Hana Hanani, Manal Bader and Farah Omar for their help and support.

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الاقرار

أنا الموقعة أدناه مقدمة الرسالة التي تحمل العنوان:

Adiabatic Coupling Constant g of the Binary Liquid Mixture Methanol – Cyclohexane

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Declaration

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

Student's Name: **اسم الطالبة:**

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List of abbreviations

I	The reduced amplitude after wave travelling
A(T)	Critical amplitude
α_λ	Sound attenuation coefficient per wavelength
$F(\omega^*)$	The scaling function
$(\frac{\partial V}{\partial P})_S$	Variation in volume with pressure at constant entropy
β_s	Isentropic compressibility
$\beta_{s,c}$	Isentropic compressibility at critical point
$\acute{S}_c$	Derivative of entropy at critical point
V_c	Critical volume
T_c	Critical temperature
$(\frac{\partial \Delta T}{\partial P})_S$	Adiabatic temperature variation
C_P	Specific heat at constant pressure
C_{Pc}	Specific heat at constant pressure at the critical point
C_{Pb}	Background specific heat at constant pressure
g	Adiabatic coupling constant
u_s	Sound velocity
$u_{s,c}$	Sound velocity at the critical point
t	Reduced temperature
$\acute{\alpha}$	Critical exponent = 0.11
$b = \frac{\alpha(\mathrm{background})}{f^2})$	Contribution of the frequency independent background absorption
f	frequency
ω_o, ω_D	Characteristic temperature - dependent relaxation rate
$C_P(t_f)$	Specific heat at constant pressure at a characteristic reduced temperature
t_f	Characteristic reduced temperature
ρ_c	Critical mass density of the binary liquid mixture
α_p	Isobaric thermal expansion coefficient
α_{pc}	Critical term in isobaric thermal expansion coefficient
α_{pb}	Background term in isobaric thermal expansion

	coefficient
$\alpha(x_c, T_c)$	The absorption coefficient at critical temperature and critical concentration.
$\alpha(x_c, T)$	The absorption coefficient at and critical concentration and any temperature
ω^*	Reduced frequency
K_B	Boltzmann's constant
ξ	Correlation length
η	Shear viscosity
$z\gamma$	A critical exponent = 1.9
x_η	A critical exponent = 0.06
rpm	Revolution per minute
cP	CentiPoise
^oC	Celsius
K	Kelvin
D	Diffusion Coefficient
x_c	Critical concentration
T_c	Critical temperature

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Abstract

The dynamic shear viscosity of the binary liquid mixture methanol - cyclohexane for different temperatures and concentrations is measured using digital viscometer with UL adapter. Shear viscosity anomaly is clearly observed near the critical temperature T_c = 45.2 ℃ and the critical concentration X_c = 30% by weight of methanol. The specific heat at constant pressure of the critical mixture methanol – cyclohexane was calculated using two scale factor universality. The dynamic scaling theory of Ferrell and Bhattacharjee is applied to the data of the ultrasonic absorption coefficients α_c at different frequencies. The linear relation of $\frac{\alpha_c}{f^2}$ versus $f^{-1.06}$ was obtained. The adiabatic coupling constant g, isobaric thermal expansion coefficient α_p and diffusion coefficient D were calculated. The experimental values of $\frac{\alpha(X_c,T)}{\alpha(X_c,T_c)}$ were plotted as a function of the reduced frequency ω^* and it showed a good agreement with the theoretical scaling function $F(\omega^*)$ presented by Ferrell and Bhattacharjee.

Chapter One

Introduction

The study of ultrasonic attenuation through absorption or dispersion is important to investigate the properties of matter in its three states. The ultrasonic velocity in a medium gives valuable information about the physical characteristics of the medium. Moreover, the ultrasonic absorption has become a powerful tool in providing important information about various inter and intra - molecular processes such as relaxation of the medium or existence of isomeric states (Jugan, 2010).

In recent years the ultrasonic absorption has extensively been applied in liquids and its mechanisms and the distribution of relaxation process in pure, binary and ternary liquid systems were realized (Jugan, 2010).

1.1 Liquid Systems

There are two types of liquid systems; first is the pure one which composed of one liquid such as olive oil, benzene methanol or coconut oil. The other one is a mixture that is composed of two or more liquids, (Santhi *et al,* 2012). Binary liquid mixture consists of two liquids that have solubility to each other at a certain temperature called critical temperature and a certain concentration called critical concentration. At the critical temperature and the critical concentration they become as one liquid; such as benzene - coconut oil, methanol - cyclohexane, benzene – tetrachloride and pentanol – nitromethane. Another type of mixtures is called ternary liquid mixture. This type is composed of three different liquids that have solubility to each other at certain concentration and certain temperature (Iwanowski, 2007).

1.2 Binary Liquid Mixture

The solubility of two liquids is a function of temperature and concentration. If two solutions are partially soluble in one another, two phases can be observed. The first is when the two liquids become one phase at a high temperature; and this is called upper consulate temperature. At lower temperatures, they will be separated. The second is when the two liquids become one phase at a lower temperature, but separated at a higher temperature this is called lower consulate temperature as in Fig. (1.1) (Stenland, 1995).

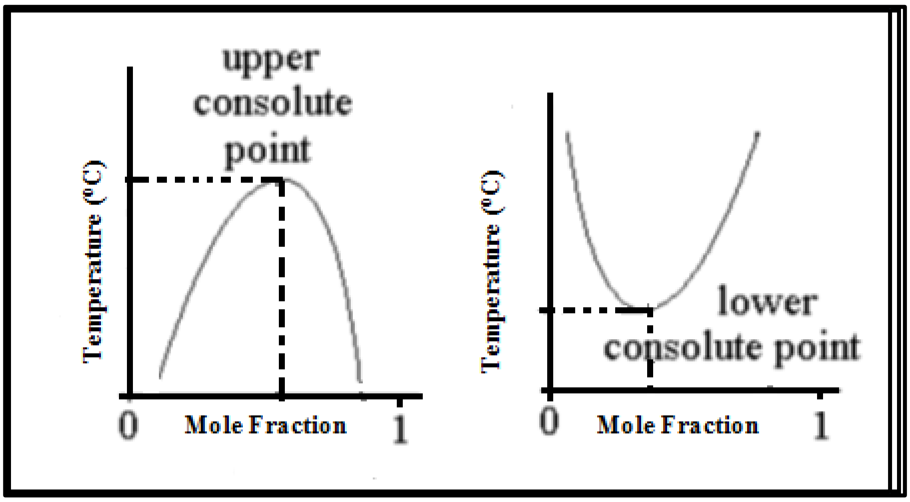

Fig. (1.1): Upper and lower critical temperatures for binary liquid mixtures (Stenland, 1995).

1.3 Literature Review

There are numerous studies which discuss the properties of pure, binary and ternary liquid mixtures using different theories, such as: mode coupling, renormalization or dynamic scaling theories.

The viscosity of methanol - cyclohexane binary liquid mixture was studied to understand kinetic process near the critical temperature. It was proved that the viscosity and its derivative with respect to temperature at the critical point become infinite (Kuskova and Matizen, 1970).

Anisimove and his team studied methanol - cyclohexane binary liquid mixture and measured the specific heat near the critical temperature. It is found that the impurities influence the character of singularity of different physical properties as the compressibility and specific heat at the critical point (Anisimove *et al*, 1972).

The specific heat at constant volume for methanol - cyclohexane binary liquid mixture was measured near the critical temperature. Some parameters were calculated such as variation of the critical temperature with respect to pressure $\frac{dT_c}{dP}$ and speed of ultrasonic waves (Anisimov *et al*, 1972).

Methanol - cyclohexane, triethylamine - water and nitrobenzene - hexane binary liquid mixtures were studied. Shear viscosity was calculated near the critical temperature for each system. It is concluded that the viscosity has finite value at the critical temperature, but it's derivative with respect to temperature become infinite at the croitical point (Kuskova and Matizen, 1973).

Bains and Berazeale had studied the properties of β,β-dichlerethyl – ether mixture based on Fixmans' theory at the critical region. It is found that the critical region increase the shear viscosity of the binary liquid mixture β,β-dichlerethyl – ether (Bains and Berazeale, 1975).

Rao and Reddy had studied the ultrasonic absorption in benzene, chloroform, cyclohexane and toluene with triethylamine binary mixtures at frequency 7.56 MHz at different concentrations (Rao and Reddy, 1977).

The ultrasonic absorption and dispersion near the critical point of a binary liquid mixture were studied over a wide range of frequencies and temperatures by Harada and his group (Harada *et al*, 1980).

Ferrell and Bhattacharjee presented a new theory of critical ultrasonic attenuation in binary liquid mixtures based on the frequency - dependent specific heat. The theoretical results are fitted with the experimental ones (Bhattacharjee and Ferrell, 1981).

The acoustic velocity and attenuation have been measured for the binary liquid mixture 3-methylpentane - nitroethane in the frequency range 1 – 17MHz and temperature range $0.09 \leq T\text{-}T_c \leq 13.5$K. The experimental data of the reduced frequency fitted with the dynamic scaling, renormalization and mode coupling theories by Garland and Sanchez. The scaling function as a function of the reduced frequency was plotted using the dynamic scaling theory. It is concluded that Ferrell and Bhattacharjee hypothesis of scaling function is in a good agreement with experimental results (Garland and Sanchez, 1983).

The acoustic velocity and attenuation have been measured for the binary liquid mixture cyclohexane - nitroethane in the frequency range 3 – 27MHz and temperature range $0.01 \leq T\text{-}T_c \leq 15$K according to the dynamic scaling theory by Garland and Sanchez (Sanchez and Garland, 1983).

Heat capacity of the binary liquid mixture 3-methyl pentane - nitroethane was measured. Parameters such as the critical exponent α, correlation length ξ and the amplitude of the heat capacity at constant pressure C_P were calculated based on the renormalization group and two - scale factor theories by Sanchez and his team (Sanchez *et al*, 1983).

The ultrasonic wave attenuation for triethylamin - water binary liquid mixture was measured according to the dynamic scaling theory at the critical temperature. The relation between ultrasonic absorption coefficient $(\frac{\alpha}{f^2})$ versus $f^{-1.06}$ was proved to be straight line according to the dynamic scaling theory. The adiabatic coupling constant (g) has been evaluated by Fast and Yun (Fast and Yun, 1985).

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).

Srivastava and Smith had prepared the binary liquid mixture of methanol - hydrocarbon and the volume change of mixing has been calculated from the experimental results (Srivastava and Smith, 1987).

Thomson and his team have 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 data of density, mole fraction and solubility for the binary liquid mixtures of n-hexane - methanol and cyclohexane - methanol and of ternary mixture as n-hexane - cyclohexane- methanol were measured over temperature range 284 – 298K. It was concluded that the impurity of water in methanol affect both ternary and binary liquid mixture (Alessi *et al*, 1989).

Ferrell found that the sound propagation produce temperature swings if the frequency is smaller than the relaxation time (Ferrel, 1989).

Sticklers' group measured the ultrasonic velocity, absorption and shear viscosity for the binary liquid mixture polyvinylpyrrolidone – water as a function of temperature and concentration. The frequency used was 21MHz and the concentration ranges from 1% to 9% by weight of polyvinylpyrrolidone while the temperature was from 20 to 45^{o}C. It has been noticed that $\frac{\alpha}{f^2}$ and viscosity values increase with concentration and decrease with temperature (Spickler *et al*, 1989).

Refractive index and density have been obtained to determine thermodynamic divergences. The triethylamine - water mixture turbidity was measured in order to calculate the correlation length and compressibility values using the two scale factor universality by Zalczer and Beysens (Zalczer and Beysens, 1990).

Abdelraziq and his group studied the ultrasonic absorption and velocity as a function of temperature and concentration, shear viscosity is studied as a function of concentration and temperature for nitrobenzene-n-hexane above the critical temperature range between 5 - 25MHz, using the dynamic scaling theory (Abdelraziq *et al*, 1990).

Woermann studied the measurements of ultrasonic attenuation as a function of temperature and frequency dependent at frequency range

9-45MHz for isobutyric acid - water mixture. In addition, the ultrasonic absorption has been measured for different ranges of frequency 0.2 - 400MHz. The spectra of relaxation time were observed above the critical temperature T_c (Woermann, 1991).

Abdelraziq and his team have measured the ultrasonic velocity and absorption for the binary liquid mixture carbon tetrachloride – coconut oil. The dynamic scaling theory was applied in the frequency range of 5 – 35MHz (Abdelraziq *et al*, 1992).

Esquivel – Sirvent and his group have studied the absorption and velocity of sound of ethylene glycol – water binary liquid mixture. The frequency used was 21MHz and the concentrations were from 1% to 9% of ethylene glycol. The shear viscosity was measured as a function of temperature (Esquivel – Sirvent *et al*, 1993)

The ultrasonic absorption coefficient α was measured for the binary liquid mixture cyclohexane – analine by Abdelraziq. The dynamic scaling theory was applied in the frequency range of 5 – 35MHz (Abdelraziq, 1996).

Heat capacity 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 team (Flewelling *et al*, 1996).

Abdelraziq and his group have measured the shear viscosity as a function of temperature for the binary liquid mixture nitrobenzene – n-heptane. The deby momentum cutoff q_D was calculated using the mode coupling theory (Abdelraziq *et al*, 1997).

Aniline - cyclohexane binary liquid mixture has been prepared; the critical part of ultrasonic attenuation was calculated from the dynamic scaling theory in frequency range 30 KHz – 3GHz by Mirzaev and Kaatze (Mirzaev and Kaatze, 2000).

Abdelraziq studied the ultrasonic absorption at 5 - 25MHz frequency range and velocity measurements above the critical temperature for perfluoromethyl cychlohexane - carbon tetrachloride (Abdelraziq, 2000).

Mirzaev and his group have used ethanol - dodecane mixture to study ultrasonic attenuation spectra between 200KHz - 500MHz frequency range around the critical temperature using the dynamic scaling theory (Mirzaev *et al*, 2000).

The adiabatic coupling constant, correlation length and diffusion coefficient were obtained for the binary mixture aniline - cyclohexane using mode coupling theory by Abdelraziq (Abdelraziq, 2001).

Abdelraziq has measured the shear viscosity for the binary mixture nitroethane – 3-methylpentane in the temperatures range $0.040 \leq T-T_c \leq 18.570K$. Debye momentum cutoff q_D and the constant A have been calculated using the mode coupling theory (Abdelraziq, 2002).

The adiabatic coupling constant (g) was calculated for both binary liquid mixtures, benzonitrile - isooctane and nitroethane – isooctane to be 0.862 and 0.356 respectively .The obtained data were compared to the dynamic scaling and renormalization group theories by Madej and Hornowski (Madej and Hornowski, 2002).

The sound velocity, density and viscosity have been measured to investigate the properties of 2-Ethoxy - Ethanol, DMSO, DMFA and DMA at 308.15K. The ultrasonic relaxation time, excess volume, adiabatic compressibility, internal pressure and acoustic impedance have been calculated by Johnson group (Johnson *et al*, 2002).

The adiabatic coupling constant (g) was derived for triethylamine – water mixture using Ferrell- Bhattacharjee dynamic scaling theory. Shear viscosity at the critical concentration near the critical temperature was compared to previous studies by Behrends and his team. They found that the critical part of specific heat at constant pressure is not smaller than the background one as predicted by Ferrell and Bhattachrjee (Behrends *et al*, 2002).

Abdelraziq has studied different binary liquid mixtures as Nitrobenzene - n-hexane, Methanol - n-heptane, Methanol - cyclohexane, Nitrobenzene - n-heptane and others. The universal quantity R was calculated for every liquid mixture. In three dimensions it has been concluded that fluid and binary mixtures transitions belong to the same class of universality "two scale factor universality, (Abdelraziq, 2003).

Behrends and his group had tested methanol- cyclohexane binary liquid system in the frame of dynamic scaling theory and the adiabatic coupling constant was calculated. It is concluded that the temperature variation is due to the g temperature dependence and thermal expansion coefficient (Behrends *et al*, 2003).

Ultrasonic spectra, shear viscosity and mutual diffusion coefficient have been measured at critical temperature and concentration for n-Pentanol - nitromethane liquid binary system. It has been noticed for viscosity and diffusion measurements that the critical part in sonic attenuation coefficient was played as a scaling factor and fit with the dynamic scaling theory. The adiabatic coupling constant for n-Pentanol - nitromethane was evaluated to be 0.03 by Iwanowski and his team (Iwanowski *et al*, 2004).

Shear viscosity, mutual diffusion coefficient and ultrasonic attenuation have been measured for nitroethane - cyclohexane mixture at different temperatures near the critical one. The adiabatic coupling constant was calculated using Ferrell and Bhattacharjee theory by Behrends and his group (Behrends *et al*, 2004).

Butyl - formate, binary liquid mixture and acoustic spectra have been investigated over the frequency range 0.1 – 150MHz and temperature 20 – 80^0C. It was showed a single relaxation term in the frequency range between 200KHz – 2MHz. Different parameters were determined as the velocity, relaxation rate, relaxation amplitude and background ultrasonic attenuation. (Mirzaev *et al*, 2005).

Acoustical attenuation and velocity were measured for three liquids; thiophene - p and m-xylenes over frequency range 0.3 – 0.5MHz, and 10MHz – 10GHz at 293.15K. The absorption was noticed to decrease when xylenes was increased and for thiophene it showed vibrational degree of freedom (Bogumil and Lezhnev, 2005).

1-Butanol in pyridine benzene was prepared; the sonic velocity, viscosity and density were measured, adiabatic compressibility, free length and internal pressure were calculated (Aral and Palaniappan, 2005).

Abdelraziq studied the ultrasonic absorption at 5-25MHz frequency range for benzene-coconut oil and hexane-β, β-dichloroethyl ether mixture at different temperatures above the critical one (Abdelraziq, 2005).

Iwanowski and his group have measured acoustical attenuation, shear viscosity, density and heat capacity for the binary mixture methanol - n-hexane. The critical part of ultrasonic attenuation was calculated to be fitted with dynamic scaling theory. The correlation length, relaxation rate and adiabatic coupling constant were calculated (Iwanowski *et al*, 2006).

Critical temperature and concentration have been determined for the binary liquid mixture triethylene glycol - monohyptyl ether. The shear viscosity and mutual diffusion coefficient were evaluated and sonic attenuation has been calculated using dynamic scaling theory (Haller *et al*, 2006).

The ultrasonic velocity and density for disopropyl ether - bromobenzene have been performed and intermolecular length, compressibility and acoustic impedance were calculated (Nath *et al*, 2006).

The scaling function for methanol - cyclohexane binary liquid mixture is in a good agreement with dynamic scaling theory. Ultrasonic attenuation and shear viscosity were measured; the correlation length, relaxation rate and adiabatic coupling constant have been calculated (Mirzaev *et al*, 2007).

The ultrasound absorption and velocity were measured for the binary liquid mixtures CS_2 - CCl_4 and CCl_4 - $CHCl_3$ over frequency range 5 – 45MHz and it has observed that $\frac{\alpha}{f^2}$ agreed with Baur - Sette relation (Karabulut and Buyer, 2007).

Shear viscosity, dynamic light scattering and ultrasonic attenuation have been set as a function of temperature near the critical one for the critical ternary system 3-methyl pentane - nitroethane - cyclohexane and the adiabatic coupling constant was calculated (Iwanowski *et al*, 2008).

The density and viscosity for diaceton alcohol - benzene and chloro - benzene were measured at 303.15, 313.15 and 323.15K (Kubendran and Baskaran, 2008).

Ultrasonic spectroscopy, quasi elastic light scattering and shear viscosity were measured for the ternary mixture methanol - n-hexane – cyclohexane. The theories of binary liquid systems as the dynamic scaling theory, renormalization group theory and dynamic light scattering were applied, correlation length and relaxation rate were calculated and the scaling function was discussed based on dynamic scaling theory (Iwanowski *et al*, 2009).

Zorebski measured the ultrasonic absorption coefficients for the 1,2-ethanediol - 1-nonanol mixture versus concentration at T = 298.15K for frequency 30-80MH. The volume viscosity was calculated from the measured properties (Zorebski, 2010).

Bhattacharjee and his group discussed the origin of sound attenuation through liquid systems around the critical point. Quasi - elastic scattering, shear viscosity and heat capacity were measured and studied theoretically according to the dynamic scaling theory (Bhattacharjee *et al*, 2010).

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

Data of ultrasonic attenuation spectra between 50KHz – 10GHz have been analyzed of nitrobenzene - n-hexane system using Ferrell and Bhattacharjee dynamic scaling theory. The bulk viscosity and relaxation rate were calculated (Mirzaev and Kaatze, 2012).

Acoustic impedance, compressibility and intermolecular length were calculated using the measurements of density and acoustical velocity for the binary liquid mixture 4bromobenzene – chlorobenzene at different frequencies (Nath, 2012).

Ultrasonic velocity and density have been measured for the binary liquid mixture anisaldehyde - alcoxy-ethanols at different temperatures. Theoretical values of sonic velocity and concentration were calculated (Begum *et al*, 2012).

Viscosity and density were measured for the liquid system pyridine with some alcohols as methanol, ethanol, n-propanol and n-butanol at different temperatures. The excess molar value and deviation in viscosity were determined (Dikio *et al*, 2012).

N-n dimethyl formide – cyclohexane - chlorobenzene ternary liquid system was performed. Density and viscosity were measured. Free length, relaxation rate, adiabatic compressibility and acoustic impedance have been calculated (Praharaj *et al*, 2012).

Ultrasonic studies, densities and viscosities of the mixture ethylamine – benzyl alcohol have been measured and some properties such as speed of sound, compressibility and molar volume were calculated at temperatures 30, 35, 40^{o}C. These values give information about intermolecular interactions and their strength (Saxena *et al*, 2013).

The ultrasonic velocity and density have been measured for the binary liquid mixtures anisic aldehyde with some esters over temperature range 303.15 – 318.15K using different models such as impedance, ideal mixing and Rao's specific velocity relations. Parameters such as intermolecular free length L_f, viscosity η, isentropic compressibility were calculated (Sandhya *et al*, 2013).

1, 3, 4-thiadiazole have been studied by Alamelumangai and Santhi. Adiabatic compressibility, intermolecular length and relaxation rate were calculated. The density and ultrasonic velocity were measured at 303.15K (Alamelumangai and Santhi, 2014).

Qasem studied the ultrasonic absorption and velocity for the binary liquid mixtures 3-methylpentane – nitroethane and nitrobenzene – n-hexane. The mode coupling theory by Fixmann is used (Qasem, 2014).

Kittany has measured the dynamic shear viscosity of the binary liquid mixture coconut oil – carbon tetrachloride. Deby parameter L was calculated using light scattering formula. The Deby momentum cutoff q_D

and noncritical shear viscosity η_o were calculated using mode coupling theory (Kittany, 2014).

Nierat and her team have studied the dynamic viscosity of olive oil as a function of temperature. The olive oil sample was from Jenin in Palestine (Nierat *et al*, 2014).

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

1.4 Objectives of the Study

The main goal of this work is to apply the dynamic scaling theory for the binary liquid mixture methanol – cyclohexane. Several thermodynamic properties will be determined for the binary mixture under study as critical heat capacity, isobaric thermal expansion coefficient, the adiabatic coupling constant, diffusion coefficient and critical sound velocity. The motivation behind this study is that the liquid system methanol – cyclohexane is very important in industry and chemical study because of the existence of hydrogen bonding in methanol which is an alcohol and this type of bonding is absent in cyclohexane which is an alkane. Up to our knowledge this binary liquid system has been studied using different theories like the mode coupling theories but rarely using the dynamic scaling theory. The adiabatic coupling constant has been calculated with its sign which has not been appeared in other researches; the effect of this constant has been discussed in this thesis.

1.5 Thesis layout

The first chapter of the thesis is the introduction which presents definition of binary liquid mixture and previous researches which are discussing the binary liquid mixtures and their properties.

Chapter two discussed the theories concerned with binary mixtures as mode coupling theories, renormalization group theory and highlighted the dynamic scaling theory of Ferrell and Bhattacharjee.

The methodology of work is presented in chapter three while in chapter four, the results were analyzed and discussed in chapter five.

Chapter two

Theory

Attenuation of sound waves may occur when the sound travels through a medium. There are two mechanisms: the absorption part that converts the acoustic energy into thermal energy and the other part is the scattering of the acoustic energy out of the sound beam. (Kinsler, 1980).

Attenuation serves as a measurement tool that leads to the formation of theories to explain physical or chemical phenomena that increases the ultrasonic intensity

The intensity of a decaying plane wave is given by:

$$I = I_0 \, e^{-\alpha Z}. \qquad (1)$$

Where, I: is the reduced intensity after wave travelling, I_0: is unattenuated intensity of the propagating wave at some location and α: is the attenuation coefficient in z direction (Kinsler, 1980).

There are different theories that have described the sound attenuation through binary liquid mixtures at the critical points. These theories are the renormalization group theory by Kroll and Ruhland, dynamic scaling theory by Ferrell and Bhattacharjee and mode coupling theories that have been proposed by Fixman and developed by Mistura, Chaban, Shiwa and Kawasaki (Honenberg and Halperin, 1977; Abdelaziq, 2001).

2.1 Mode Coupling Theories:

Mode coupling theories are successful to study the sound absorption and dispersion for dynamic critical phenomena, especially for pure and simple fluids and binary liquid mixtures (Harada *et al*, 1980). It provides different thermodynamic properties for the desired mixtures such as the decay rate, frequency dependent viscosity and correlation length (Harada *et al*, 1980).

The theory has a general expression for sound attenuation at critical concentration:

$$\frac{\alpha_\lambda}{u^2(\omega)} = \pi A(T) F(\omega *) \tag{2.1.1}$$

Where α_λ: is the sound attenuation coefficient per wavelength, u(ω): is velocity of sound, A(T): is critical amplitude and F(ω*): is the scaling function (Kawasaki, 1970).

2.2 Renormalization Group Theory:

The theory of renormalization group deals with critical exponents in order to calculate different thermodynamic properties for the binary liquid mixtures; the critical exponents' computation depends on the spatial parameter d and number of components of the system n (Siggia *et al*, 1976; Hohenberg and Halperin and Iwanowski, 2007).

2.3 Dynamic Scaling Theory:

The dynamic scaling theory has been developed by Ferrell and Bhattacharjee. A multiple of thermodynamic properties have been calculated by studying the attenuation of ultrasonic waves through liquids. (Hohenberg and Halperin, 1977; Abdelraziq, 1999; Iwanowski, 2007).

The study of the propagation velocity plays an important role to understand the sound attenuation at the critical point. This allows the understanding the sound absorption and dispersion near the consolute point (Iwanowski, 2007). In order to find the velocity due to the sound propagation, the variation in volume with pressure $(\frac{\partial V}{\partial P})_S$ at constant entropy S should be determined, this leads to a new parameter called the isentropic compressibility β_s is given by

$$\beta_s = \beta_{s,c} + \frac{\acute{S}_c}{V_c}(\frac{\partial \Delta T}{\partial P})_S \qquad (2.3.1)$$

Where $\beta_{s,c}$: is the isentropic compressibility at critical point, $\acute{S}_c$: is the derivative of entropy at critical point and V_c: is the critical volume (Iwanowski, 2007 ; Bhattacharjee *et al*, 2010).

$\Delta T = T - T_c$, whereT_c: is the critical temperature.

The adiabatic temperature variation $(\frac{\partial \Delta T}{\partial P})_S$ can be expressed as:

$$(\frac{\partial \Delta T}{\partial P})_S = -\frac{T_c}{C_P}\acute{S}_c = -g\frac{V_c}{C_P} \qquad (2.3.2)$$

Where: C_P: is the specific heat of the mixture and g: is the adiabatic coupling constant and equals to $\frac{T_c}{V_c}\acute{S}_c$.

The adiabatic coupling constant gives a notation about the coupling between the critical density fluctuation and sound wave propagation (Bhattacharjee and Ferrell, 1981; Iwanowski, 2007; Bhattacharjee *et al,* 2010).

The sound wave velocity can be described in terms of the adiabatic coupling constant, critical temperature and specific heat as:

$$u_s = u_{s,c} + \frac{g^2\, u_{s,c}^3}{2T_cC_P} \qquad (2.3.3)$$

Where: u_s : is the sound velocity and $u_{s,c}$: is the sound velocity at the critical point (Bhattacharjee and Ferrell, 1981; Iwanowski, 2007; Bhattacharjee *et al*, 2010).

Ferrell and Bhattacharjee supposed that specific heat is dependent on frequency (ω), so the velocity can be rewritten as:

$$u_s = u_{s,c} + \frac{g^2\, u_{s,c}^3}{2T_c C(\omega)_P} \tag{2.3.4}$$

(Bhattacharjee and Ferrell, 1981; Iwanowski, 2007; Bhattacharjee *et al*, 2010)

The specific heat can also be written in terms of the reduced temperature as:

$$C_P = C_{Pc} t^{-\acute{\alpha}} + C_{Pb} \tag{2.3.5}$$

Where: C_{Pc}: is the specific heat at constant pressure at the critical point, t: is the reduced temperature = $\frac{T-T_c}{T_c}$ $\acute{\alpha}$: is a critical exponent = 0.11 and C_{Pb}: is the background specific heat (Bhattacharjee and Ferrell, 1981; Abdelraziq, 1999; Iwanowski, 2007; Bhattacharjee *et al*, 2010).

Based on the ultrasonic attenuation Ferrell and Bhattacharjee have proposed the linear relation between $\frac{\alpha(x_c,T_c)}{f^2}$ and $f^{-1.06}$, where: $\alpha(x_c, T_c)$: is the absorption coefficient at critical temperature and concentration and f: is the frequency as:

$$\frac{\alpha(x_c,T_c)}{f^2} = Sf^{-1.06} + b \tag{2.3.6}$$

Where: b: is the contribution of the frequency independent background absorption ($\frac{\alpha(\text{background})}{f^2}$) and the value of S can be represented as:

$$S = [\frac{\pi^2 C_{pc} g^2 v_c \acute{\alpha}}{2z\,\gamma T_c\; C_p^2(t_f)}]\; [\frac{a\omega_0}{2\pi}]^{\acute{\alpha}/z\gamma} \qquad (2.3.7)$$

Where: zγ: is a critical exponent = 1.9, a = $\left(\frac{\omega}{\omega_o}\right)$ $t_f^{-1.9}$, ω_o: is a characteristic temperature - dependent relaxation rate and $C_P(t_f)$: is the specific heat at a characteristic reduced temperature t_f (Abdelraziq, 1999; Iwanowski, 2007; Bhattacharjee *et al*, 2010).

The adiabatic coupling constant g is presented to verify the subdivision in attenuation spectra into the critical contribution and the sophisticated background contribution. It depends on the pressure, temperature and thermal expansion coefficient. The adiabatic coupling constant according to thermodynamic relation is given by:

$$g = \rho_c C_P\, (\frac{dT_c}{dP} - \frac{T\alpha_p}{\rho C_P}) \qquad (2.3.8)$$

Or

$$g = (\frac{C_{pb}\alpha_{pc}T_c}{C_{pc}}) - \alpha_{pb}T \qquad (2.3.9)$$

Where: ρ_c: is the critical mass density of the binary liquid mixture and α_p: is isobaric thermal expansion coefficient which can be expressed as:

$$\alpha_p = \alpha_{pc}t^{-\acute{\alpha}} + \alpha_{pb} \qquad (2.3.10)$$

Where: α_{pc} and α_{pb} are the critical and background terms in isobaric thermal expansion coefficient and $\acute{\alpha}$: is a critical exponent = 0.11 (Abdelraziq, 1999; Iwanowski, 2007; Bhattacharjee *et al*, 2010).

The theory indicates that $\frac{\alpha}{\alpha_c}$ should be a function of the reduced frequency ω* and should scale with the scaling function F(ω*).

Where: $\alpha = \alpha(x_c, T)$: is the absorption coefficient at critical concentration and temperature T and $\alpha_c = \alpha(x_c, T_c)$: is the absorption coefficient at critical temperature and critical concentration.

The expression for the critical term of the absorption as a function of reduced frequency ω^* is

$$\frac{\alpha}{\alpha_c} = F(\omega^*) = (1+ \omega^{*-0.5})^{-2} \tag{2.3.11}$$

The absorption coefficient $\alpha(\text{crit},\omega,T)$ can be expressed as a function of reduced frequency ω^*,

$$\omega^* = \frac{\omega}{\omega_D} = \frac{2\pi f}{\omega t^{z\gamma}} \tag{2.3.12}$$

Where ω_D: is the temperature dependent characteristic relaxation rate; which is given by

$$\omega_D = \frac{K_B T}{3\pi\, \eta \xi^3} = \frac{K_B T_c}{3\pi\, \eta_0\, \xi_0^3}\, t^{z\gamma} = \omega_o t^{z\gamma} \tag{2.3.13}$$

Where: ω_D: is the characteristic temperature-dependence relaxation rate, K_B: is Boltzmann's constant, ξ: is correlation length and η: is shear viscosity.

Where:

$$\omega_o = 2D_o \xi_o^{-2} \tag{2.3.14}$$

Where: D_o: is the diffusion coefficient in $\frac{cm^2}{s}$

The correlation length is given by:

$$\xi = \xi_0 t^{-\gamma} \tag{2.3.15}$$

And the shear viscosity is also given by:

$$\eta = \eta_0 t^{-x_{\eta}^{\gamma}} \qquad (2.3.16)$$

Where $x_\eta = 0.06$ is the critical exponent (Bhattacharjee and Ferrell, 1981; Abdelraziq, 1999; Iwanowski, 2007; Bhattacharjee *et al*, 2010).

Chapter Three

Methodology

The sample of the binary liquid mixture of methanol – cyclohexane has been prepared in the laboratory at different concentrations from 15% to 90% of methanol. The viscosity of different concentrations was measured at various temperatures. The experimental data were fitted and the critical temperature and concentration were obtained.

The dynamic scaling theory is applied and different properties are calculated; such as the specific heat, the thermal coefficient, the adiabatic coupling constant g, critical sound velocity and reduced frequency at different frequencies. The scaling function for the binary mixture methanol – cyclohexane is plotted to fit with the theory of dynamic scaling.

3.1 Experimental Apparatus

3.1.1 Viscosity Apparatus

A Brookfield Digital Viscometer Model DV-I+ which measures the viscosity of a fluid in centipoise with accuracy $\pm 1\%$ has been used; with set of seven spindles (RV Spindle Set) and UL-ADAPTER. The speeds of the rotated spindle are in two sets. The first one is 0.0, 0.5, 1.0, 2.0, 2.5, 4, 5, 10, 20, 50 and 100 rmp; the second one is 0.0, 0.3, 0.6, 1.5, 3, 6, 12, 30 and 60 rmp. The range of the viscosity is from 10^2 up to 1.33×10^7cP (Brookfield, 1999).

The UL-ADAPTER at speed 100 rpm was used to determine the viscosity of the binary liquid mixture methanol – cyclohexane for different concentrations at various temperatures.

Fig. (3.1): Brookfield Digital Viscometer Model DV-I+

3.1.2 Temperature Apparatus

The temperature was measured using Digital Prima long Thermometer. The accuracy of this apparatus is ±1% and the range of the temperature it measures from -20 to 100^{o}C.

Julabo F25-MV Refrigerated and Heating Circulator with accuracy ±1% is used to control the temperature of the sample in the UL-ADAPTER.

Fig. (3.2): Digital Prima Long Thermometer.

Fig. (3.3): Julabo F25-MV Refrigerated and Heating Circulator

3.1.3 Density Apparatus

The density of the liquid was measured using a pycnometer of 10ml.

Analytical balance HR-200 with accuracy ±0.0005% used to measure the mass.

The density for the critical mixture methanol – cyclohexane has been measured at different temperatures above the critical one.

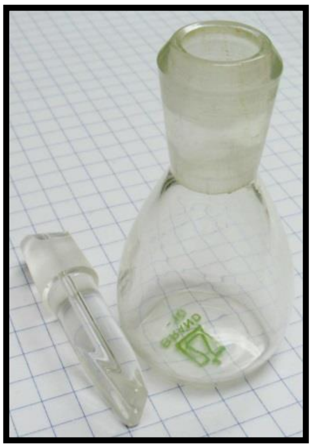

Fig. (3.4): Pycnometer of 10ml for density measurement.

Fig. (3.5): Analytical balance HR-200 to measure the mass.

3.1.4 Sound velocity Apparatus

The sound velocity of the critical sample of the binary liquid mixture methanol – cyclohexane was measured using ultrasonic thickness gauge instrument.

Fig. (3.6): Ultrasonic thickness gauge for sound velocity measurements.

3.2 Procedure

3.2.1 Preparation of the Mixture Methanol – Cyclohexane

1- The density for both methanol and cyclohexane separately has been measured at room temperature using the pycnotmeter. The mass of empty pycnometer was measured then when the pycnometer was filled with the mixture the mass was measured. The two masses was subtracted and the result is the mass of the liquid. The density was calculated by dividing the mass of the liquid by the volume of the pycnometer which was for methanol 0.7388 $\frac{\mathrm{gm}}{\mathrm{cm}^3}$ and cyclohexane 0.7307$\frac{\mathrm{gm}}{\mathrm{cm}^3}$.

2- The preparation of the mixture at various concentration [percent by weight] is done using the formula below:

$$x\% = \frac{\rho_x V_x}{\rho_x V_x + \rho_y V_y} = \frac{W_x}{W_x + W_y}$$

Where, ρ: is the density, V: is the volume, x: is the liquid which the percentage is with respect to it, y: is the second liquid and W: is the weight of the sample.

The total volume of the sample was 20ml the concentrations were taking by weight of methanol as: 15%, 20%, 30%, 40%, 50%, 60%, 70%, 80% and 90%. Each sample was kept in an appropriate container.

3.2.2 Viscosity Measurements

The UL-ADAPTER spindle was used. The sample was put in the jacket of the viscometer and the spindle speed was set at 100rpm. The values of viscosity (cP) are taken at different temperatures. The temperature of the sample was controlled by Julabo F25-MV Refrigerated and Heating Circulator and measured by Digital Prima Long Thermometer.

3.2.3 Data Analysis:

The obtained data of viscosity were tabulated and analyzed using excel program. The relation between viscosity of the binary mixture methanol –

cyclohexane and temperature for each concentration was found using excel program.

Data from literature review of the ultrasonic absorption coefficient (at the critical temperature and concentration) at different frequencies [5, 7, 10, 15, 25, 35, 45MHz] for methanol – cyclohexane were taken. The data were fitted using excel program by plotting $\frac{\alpha_c}{f^2}$ versus $f^{-1.06}$. Absorption coefficients at the critical concentration and any temperature data were taken at different frequencies [5 and 25MHz]. The relation of $\frac{\alpha}{f^2}$ versus T (^{o}C) was plotted and the temperature of the half of the maximum value was determined for each frequency.

The equations of the dynamic scaling theory were applied and various properties were calculated for the binary mixture as: adiabatic coupling constant, thermal coefficient, diffusion coefficient, sound velocity and reduced frequency. The specific heat of the binary mixture was evaluated using the two scale factor universality. The scaling function for methanol – cyclohexane was plotted and compared with the theoretical one according to the dynamic scaling theory.

Chapter Four

Results and Analysis

4.1 Viscosity Measurements

The viscosity values for the binary liquid mixture methanol – cyclohexane have been measured for different concentrations at different temperatures which are given in Table (4.1).

Table (4.1): Shear viscosity measurements at different temperatures and concentrations for the binary liquid mixture methanol – cyclohexane.

T (^{o}C)	**Concentration by weight of methanol**								
	15%	20%	30%	40%	50%	60%	70%	80%	90%
44.0		0.485	0.74	0.439					
45.0		0.467	0.77	0.426				0.74	
45.2		0.466	0.83	0.423			0.70	0.61	0.80
45.5	0.61	0.477	0.80	0.429		0.77	0.67		0.76
45.8		0.473	0.77	0.424		0.74	0.67		0.77
46.0	0.58	0.470	0.77	0.424	0.74				0.74
46.2	0.55	0.468	0.77	0.424		0.70			0.70
46.5		0.466	0.74	0.423		0.67			0.67
46.8		0.462	0.67	0.423	0.70				0.64
47.0		0.455	0.67	0.421	0.67		0.64		0.61
47.2	0.51	0.452	0.61	0.418	0.67		0.64		0.58
47.5		0.451	0.61	0.414		0.67			0.55
47.8		0.448	0.58	0.412		0.64			
48.0	0.48	0.449	0.58	0.411		0.61	0.58		
48.2	0.45	0.446	0.58	0.411		0.58	0.58	0.51	
48.5	0.44	0.443	0.55	0.399		0.45		0.48	
48.8		0.438	0.54	0.397		0.45		0.45	
49.0		0.436		0.401		0.45	0.61	0.42	
49.2							0.61	0.42	
49.5								0.42	
49.8			0.51					0.38	
50.0			0.51					0.38	0.45
51.0					0.64			0.38	
52.0			0.48		0.64	0.45		0.35	

The dynamic shear viscosity measurements in (centiPoise) as a function of the temperature in (^{o}C) are presented for each concentration from Fig. (4.1) to Fig. (4.9).

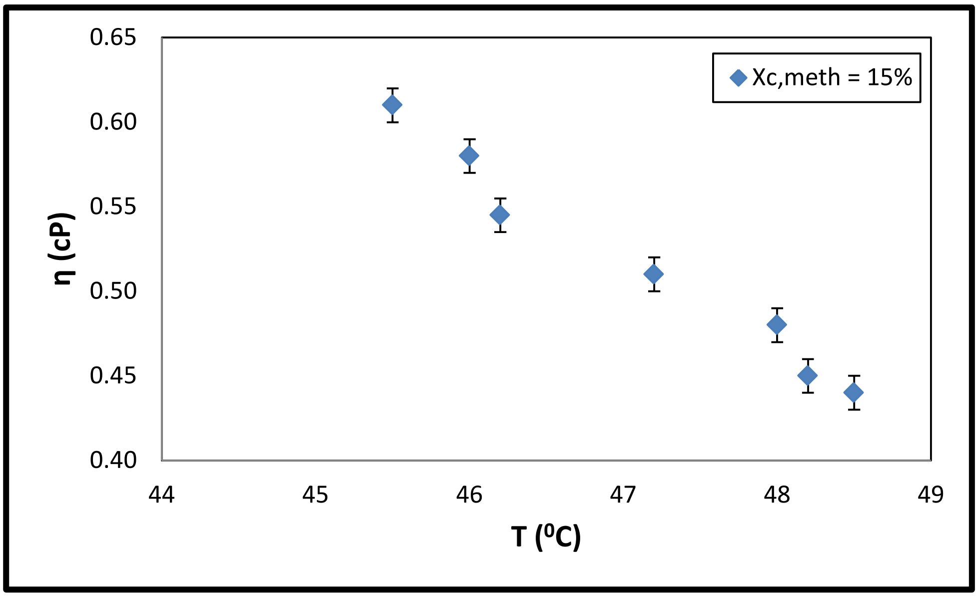

Fig. (4.1): The dynamic shear viscosity of methanol – cyclohexane as a function of temperature at concentration 15% by weight of methanol.

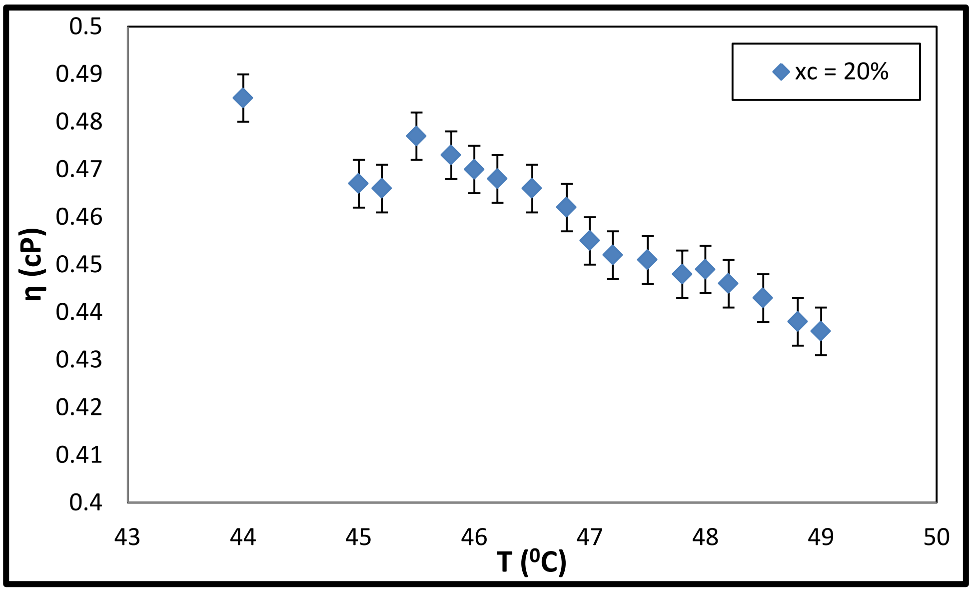

Fig. (4.2): The dynamic shear viscosity of methanol – cyclohexane as a function of temperature at concentration 20% by weight of methanol.

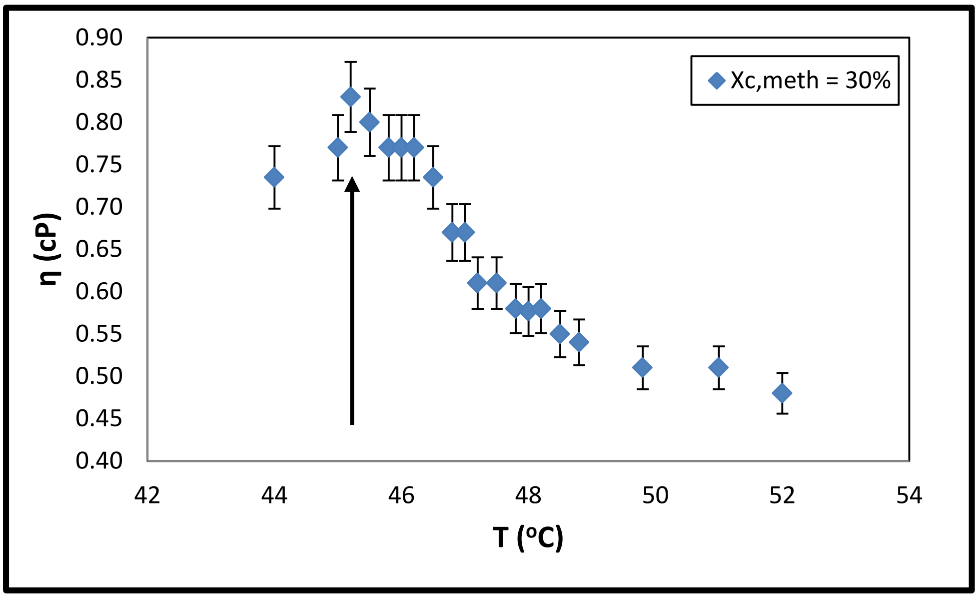

Fig. (4.3): The dynamic shear viscosity of methanol – cyclohexane as a function of temperature at concentration 30% by weight of methanol.

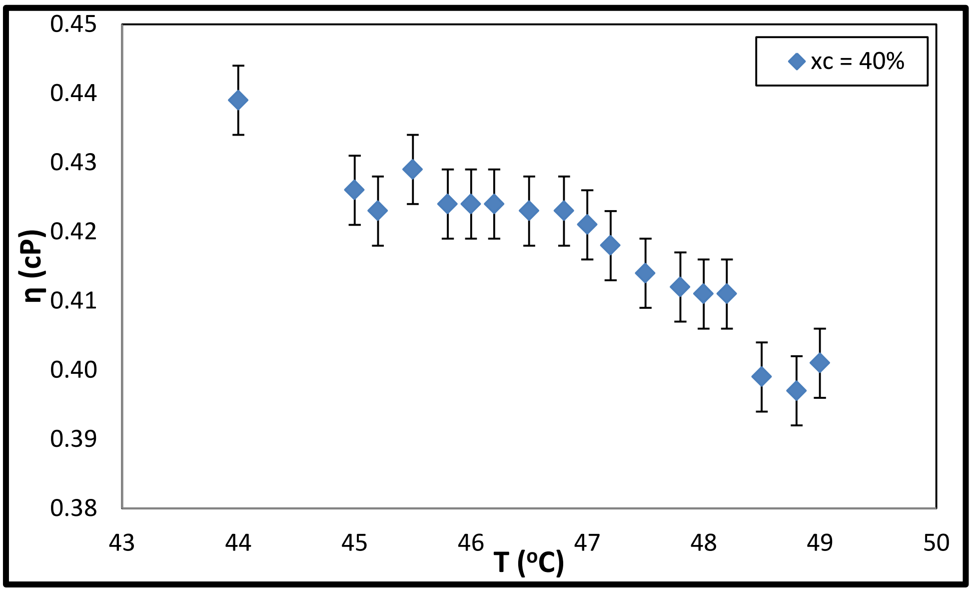

Fig. (4.4): The dynamic shear viscosity of methanol – cyclohexane as a function of temperature at concentration 40% by weight of methanol.

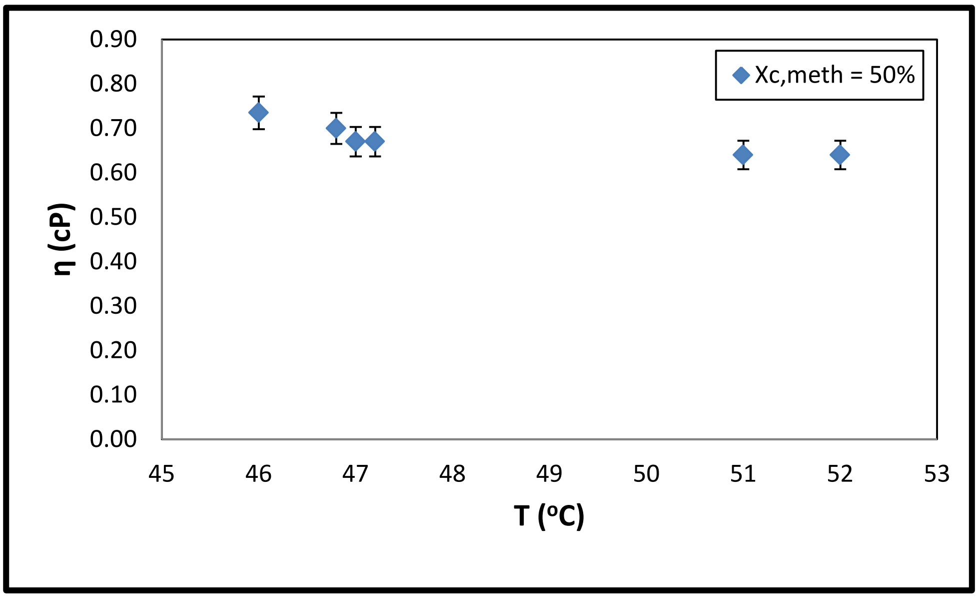

Fig. (4.5): The dynamic shear viscosity of methanol – cyclohexane as a function of temperature at concentration 50% by weight of methanol.

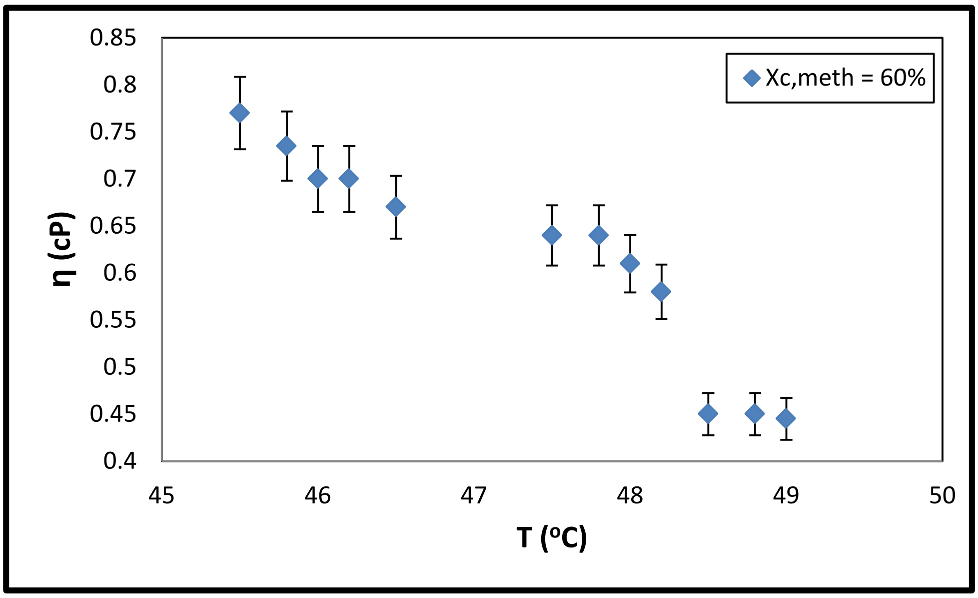

Fig. (4.6): The dynamic shear viscosity of methanol – cyclohexane as a function of temperature at concentration 60% by weight of methanol.

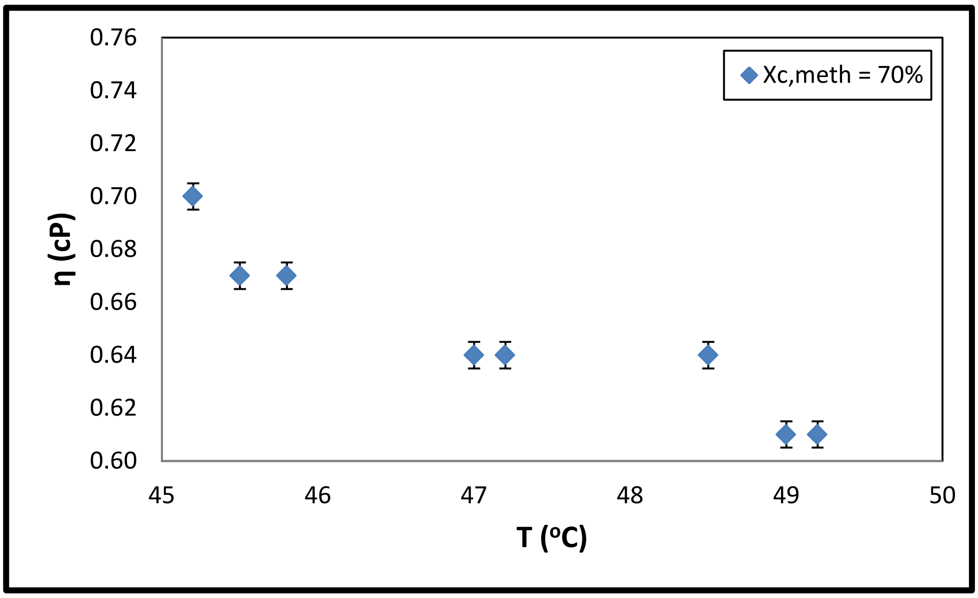

Fig. (4.7): The dynamic shear viscosity of methanol – cyclohexane as a function of temperature at concentration 70% by weight of methanol.

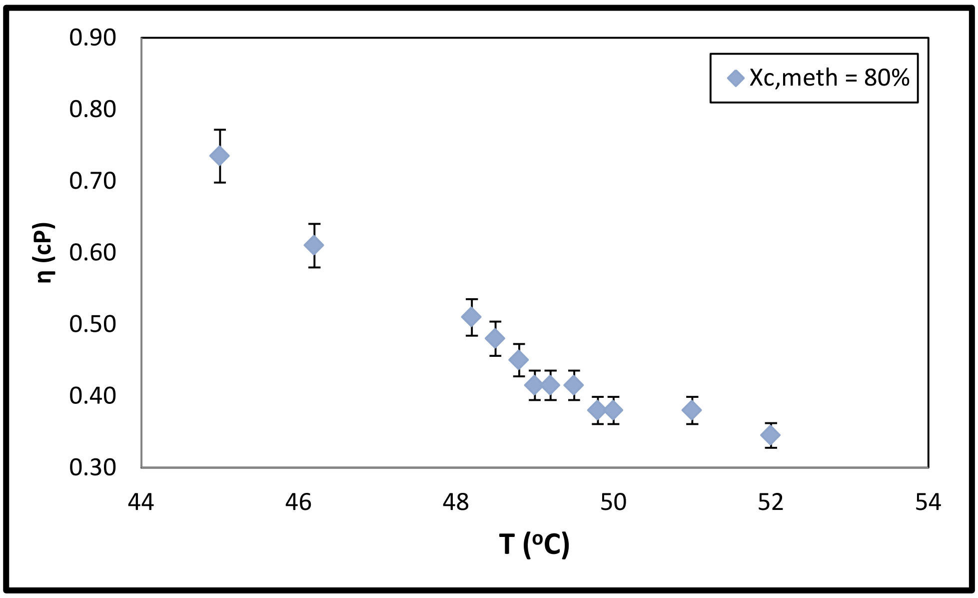

Fig (4.8): The dynamic shear viscosity of methanol – cyclohexane as a function of temperature at concentration 80% by weight of methanol.

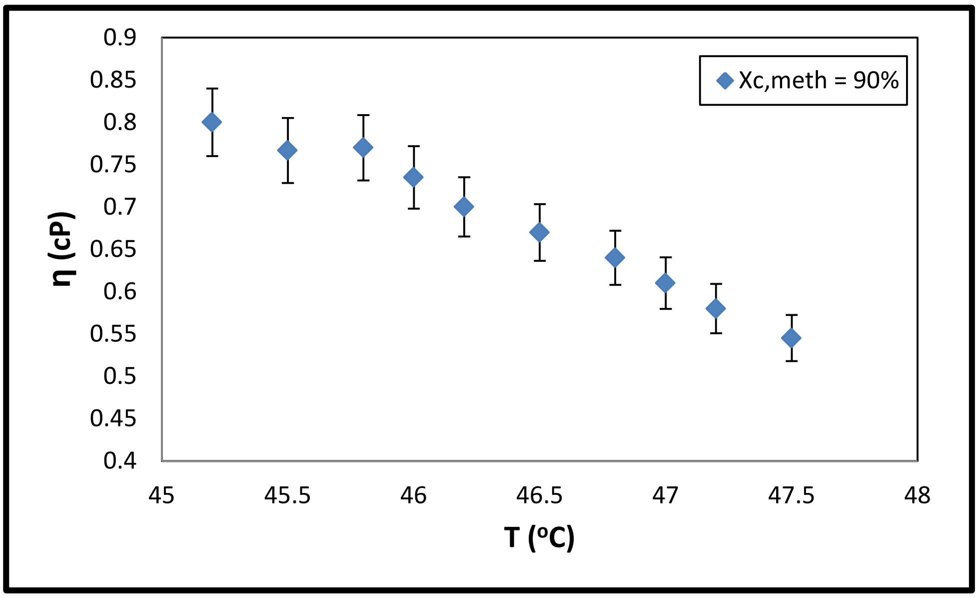

Fig. (4.9): The dynamic shear viscosity of methanol – cyclohexane as a function of temperature at concentration 90% by weight of methanol.

The experimental results of the dynamic shear viscosity of methanol – cyclohexane mixture showed an observed anomaly in Fig. (4.3). The critical concentration is 30% by weight of methanol and the critical temperature is determined at the highest value of the dynamic viscosity. The highest value of the shear viscosity is 0.83cP at concentration of 30% of weight by methanol and temperature 45.2^{o}C which is the critical one.

4.2 Specific Heat Calculation

The specific heat at constant pressure at the critical temperature is calculated using the two scale factor universality.

The universal constant R is given by:

$$R = \xi_o \{\frac{\acute{\alpha}\rho_c C_{pc}}{K_B}\}^{\frac{1}{3}} = 0.27 \qquad (4.2.1)$$

Where: $\acute{\alpha} = 0.11$, $K_B = 1.3806 \times 10^{-23} \frac{J}{K}$ and $\xi_o = 3.24 \times 10^{-10}$ m (Jacobs, 1986).

The density ρ_c of the critical mixture methanol – cyclohexane was measured at different temperatures above the critical point. The measured densities at different temperatures are given in Table (4.2).

Table (4.2): Values of density at different temperature above the critical point for the binary liquid mixture methanol – cyclohexane.

T (^oC)	**ρ ($\frac{gm}{cm^3}$)**
45.2	0.7695
45.6	0.7612
46.0	0.7596
46.4	0.7591
46.8	0.7581
47.2	0.7560
47.6	0.7532
48.0	0.7519

The critical density ρ_c at critical temperature and concentration equals to $0.7695\frac{gm}{cm^3}$.

Using equation (4.2.1) the critical specific heat at constant pressure C_{pc} for the critical mixture of methanol – cyclohexane can be calculated to be C_{pc} = $94.24\frac{J}{K.Kg}$

4.3 Calculation of the Adiabatic Coupling Constant g

The adiabatic coupling constant for methanol – cyclohexane critical mixture is calculated by using the definition

$$g = \rho_c C_P \left(\frac{dT_c}{dP} - \frac{T\alpha_p}{\rho C_P}\right) \qquad (4.3.1)$$

Where:

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

And

$$\alpha_p = \alpha_{pc} t^{-\acute{\alpha}} + \alpha_{pb} \qquad (4.3.3)$$

The thermal expansion coefficient α_p can be determined by using equation (4.3.2) where $\frac{d\rho^{-1}}{dT}$ is estimated from the linear fit of ρ^{-1} at various temperatures.

The data of the density and its inverse are presented in Table (4.3) at different temperatures above the critical point.

Table (4.3): The mass density and its reciprocal values at different temperatures for the critical mixture methanol – cyclohexane.

T (^{o}C)	**Mass density (ρ) (gm/cm^3)**	**ρ^{-1} (cm^3/gm)**
45.2	0.7695	1.2995
45.6	0.7612	1.3137
46.0	0.7596	1.3165
46.4	0.7591	1.3173
46.8	0.7581	1.3191
47.2	0.7560	1.3228
47.6	0.7532	1.3277
48.0	0.7519	1.3300

The data of the reciprocal of the density is fitted with the corresponding temperatures and the slope is determined to be the value of $\frac{d\rho^{-1}}{dT}$

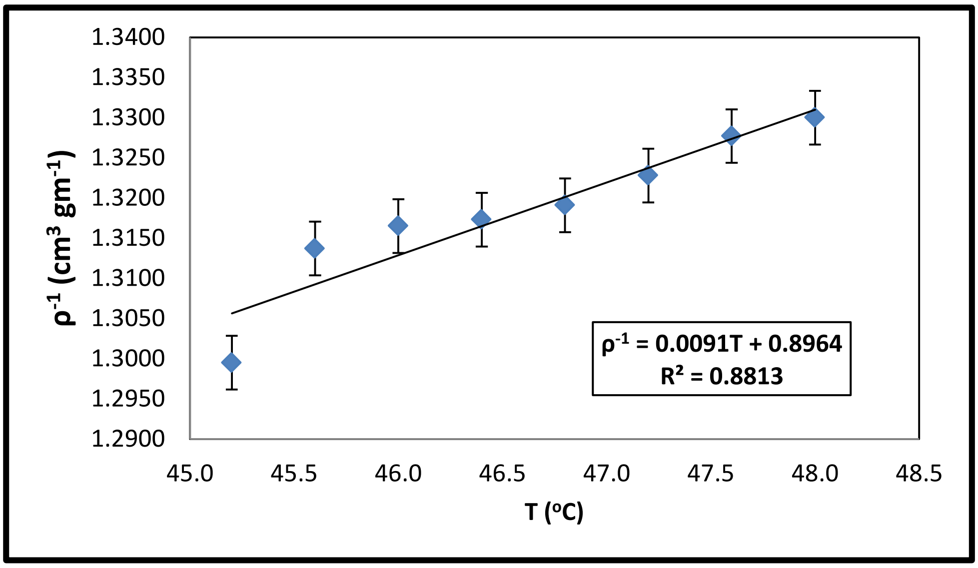

Fig. (4.10): The reciprocal of density for the critical mixture methanol – cyclohexane as function of temperature.

The slope from Fig. (4.10) is $\frac{d\rho^{-1}}{dT} = 9.1\times 10^{-3}\,\frac{cm^3}{gm.\,^oC}$

The critical and background thermal expansion coefficients can be evaluated by plotting the isobaric thermal expansion coefficient α_p versus $t^{-\acute{\alpha}}$, where $t = \frac{T - T_c}{T_c}$.

The values of α_p is calculated by multiplying the density at each temperature with the value of $\frac{d\rho^{-1}}{dT}$. The corresponding values of α_p which is $\alpha_p = \rho(\frac{d\rho^{-1}}{dT})$ are presented in Table (4.4).

Table (4.4): The isobaric thermal expansion coefficient at different temperatures for the critical mixture methanol – cyclohexane.

$\alpha_p \times 10^{-3}(\frac{1}{^oC})$	**T (^{o}C)**	$t^{-\acute{\alpha}}$
6.8510	45.6	1.6820
6.8360	46.0	1.5586
6.8320	46.4	1.4906
6.823	46.8	1.4441
6.804	47.2	1.4091
6.7790	47.6	1.3812
6.7670	48.0	1.3579

The data of the thermal expansion coefficient α_p are fitted linearly versus the $t^{-\acute{\alpha}}$ as in Fig. (4.11)

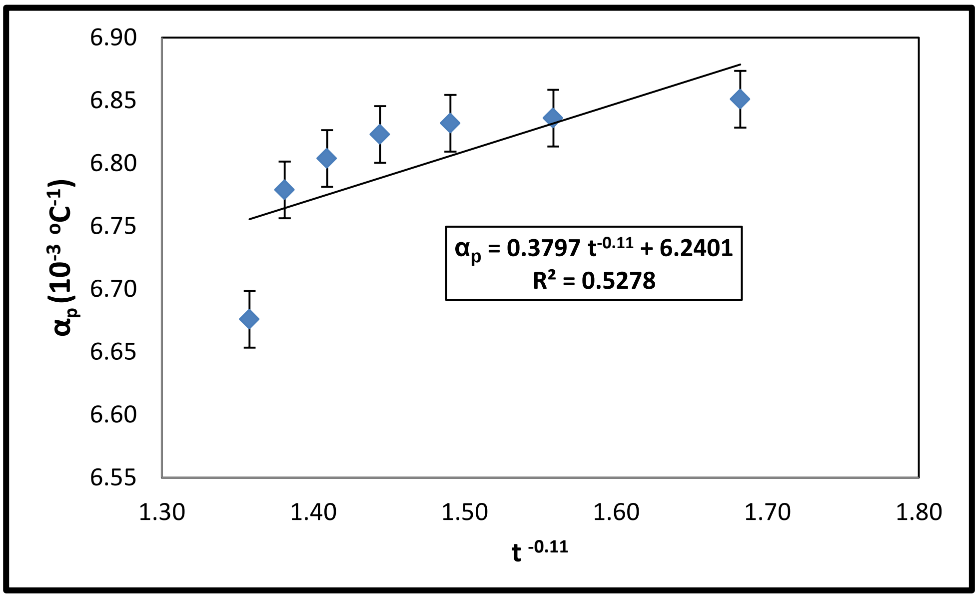

Fig. (4.11): The thermal coefficient for the critical mixture methanol – cyclohexane as function of t $^{-0.11}$.

The slope of Figure (4.7) represents the critical isobaric thermal expansion coefficient (α_{pc}) = $3.797 \times 10^{-4}\ ^{o}C^{-1}$ according to equation (4.3.3). The intercept of the line represents the background isobaric thermal expansion coefficient (α_{pb}) = $6.2401 \times 10^{-3}\ ^{o}C^{-1}$.

The value of the adiabatic coupling constant at the critical temperature can be calculated using equation (4.3.1) $g = \rho_c C_P \left(\frac{dT_c}{dP} - \frac{T\alpha_p}{\rho C_P}\right)$

Using $\rho_c = 0.7695\frac{gm}{cm^3}$, $C_P = 9.4239 \times 10^5 \frac{erg}{^oC\,.gm}$, $\frac{dT_c}{dP} = 3.4 \times 10^{-8}\frac{cm^2\ ^oC}{dyne}$

(Kuskova *et al*, 1970), T = 45.2°C and $\alpha_p = \rho \times 9.1 \times 10^{-3}\ ^{o}C^{-1}$

g = - 0.29

4.4 Ultrasonic Attenuation Results

The binary liquid mixture methanol – cyclohexane has a critical temperature at 45.2°C. The absorption measurements were made for the frequencies 5, 10 and 25MHz in the critical concentration sample of 30%

by weight of methanol above the critical temperature and the corresponding data are shown in Table (4.5) as:

Table (4.5): The absorption coefficient at different temperatures and two frequencies 5 and 25MHz for the critical mixture methanol – cyclohexane.

T (^oC)	**$\alpha(X_c, T)$ ($\frac{dB}{cm}$)**	**$\frac{\alpha}{f^2} \times 10^{-12}(cm^{-1}s^2)$ At 5MHz**	**$\frac{\alpha}{f^2} \times 10^{-12}(cm^{-1}s^2)$ At 25MHz**
45.2	0.475	1.900	0.752
46.0	0.390	1.560	0.672
48.0	0.320	1.280	0.642
49.0	0.300	1.200	0.576
50.0	0.270	1.080	0.544
51.0	0.240	0.960	0.496

The temperature dependence of the absorption $\frac{\alpha}{f^2}$ for the critical mixture methanol – cyclohexane at two different frequencies [5 and 25MHz] is presented in Fig. (4.12).

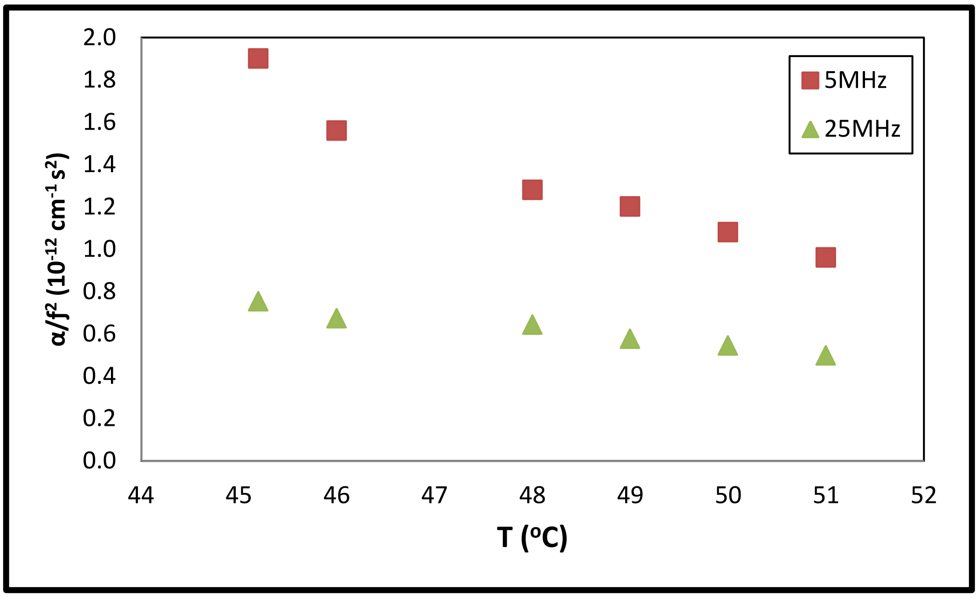

Fig. (4.12): The absorption coefficient $\frac{\alpha}{f^2}$ at frequencies 5 and 25MHz for the critical mixture methanol – cyclohexane as function of temperature.

A characteristic temperature t_f and the corresponding reduced temperature can be determined from Fig. (4.12). The temperature at the half of the highest value is determined for each frequency. At frequency of 5MHz the maximum value of $\frac{\alpha}{f^2}$ is $1.9 \times 10^{-12} cm^{-1} s^{-2}$, the half value is 0.95 $\times 10^{-12} cm^{-1} s^{-2}$ and the corresponding temperature is 51°C. At 25MHz the maximum value of $\frac{\alpha}{f^2}$ is $0.752 \times 10^{-12} cm^{-1} s^{-2}$, the half value is $0.376 \times 10^{-12} cm^{-1} s^{-2}$ and the corresponding temperature is 52°C. The obtained values of the characteristic temperature at each frequency is used to evaluate the dimensionless constant a = $(\frac{\omega}{\omega_o}) t_f^{-z\gamma}$.

Ferrell and Bhattacharjee in the theory of the dynamic scaling proposed that the relation between $\frac{\alpha_c}{f^2}$ and $f^{-1.06}$ is fitted linearly for different values of frequency at the critical concentration and temperature. Values of the critical absorption coefficient α_c at different frequencies from 5 – 45MHz are given in Table (4.6).

Table (4.6): The absorption coefficient at different temperatures and frequencies from 5-45MHz for the critical mixture methanol – cyclohexane.

f (MHz)	$\alpha\,(\frac{dB}{cm})$	$\frac{\alpha_c}{f^2} \times 10^{-15} (cm^{-1}s^2)$	$f^{-1.06} \times 10^{-8}\ (s^{1.06})$
5	0.475	19.000	7.927
7	0.799	16.306	5.549
10	1.480	14.800	3.802
15	2.250	10.000	2.474
21	3.970	9.002	1.732
25	4.690	7.504	1.439
35	8.580	7.004	1.008
45	13.160	6.499	0.772

The data of the absorption coefficient at critical temperature and concentration $\frac{\alpha_c}{f^2}$ are plotted versus $f^{-1.06}$ and presented in Figure (4.13).

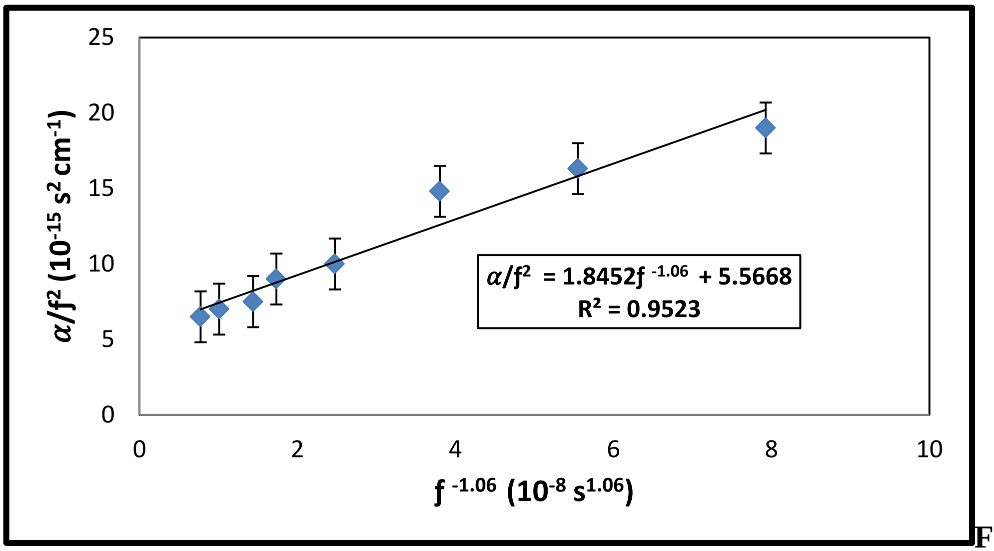

Fig. (4.13): The absorption coefficient $\frac{\alpha_c}{f^2}$ for critical mixture methanol – cyclohexane as function of $f^{-1.06}$.

The slope from Fig. (4.13) represents the critical part of the attenuation is to be 1.8452×10^{-7} $\mathrm{cm^{-1}s^{0.94}}$ and the intercept which represents the frequency – independent background term of $\frac{\alpha_c}{f^2}$ which is 5.5668×10^{-15} $\mathrm{cm^{-1}s^{2}}$.

The magnitude of the slope from Fig. (4.13) is expressed as:

$$\text{Slope (S)} = \left[\frac{\pi^2 C_{pc} g^2 u_c\, \acute{\alpha}}{2z\,\gamma T_c\; C_p^2(t_f)}\right]\left[\frac{a\omega_0}{2\pi}\right]^{\acute{\alpha}/z\gamma} = 1.8452 \times 10^{-7}\ \mathrm{cm^{-1}s^{0.94}}. \quad (4.4.1)$$

The characteristic temperature – dependent relaxation rate ω_0 is calculated from equation:

$$\omega_D = \frac{K_B T}{3\pi\,\eta\xi^3} = \frac{K_B T_c}{3\pi\,\eta_0\,\xi_0^3}\,t^{z\gamma} = \omega_0 t^{z\gamma} \qquad (4.4.2)$$

Where, $\omega_0 = \frac{K_B T_c}{3\pi\,\eta_0\,\xi_0^3} = \frac{1.3806 \times 10^{-23} \times 318.35}{3\pi \times 8.3 * 10^{-4} \times (2.5 \times 10^{-10})^3} = 3.5959 \times 10^{10}\ \mathrm{s^{-1}}$.

The value of the dimensionless constant a is calculated from the equation:

$$a = \left(\frac{\omega}{\omega_o}\right) t_f^{-1.9} \qquad (4.4.3)$$

Where

$$\omega = 2\pi f \qquad (4.4.4)$$

The values of the dimensionless constant a from Fig. (4.12) at the frequencies 5 and 25MHz are:

a (5MHz) = $\frac{5*10^{6}}{3.5959*10^{10}}(0.1283)^{-1.9}$ = 6.8772×10^{-3} and

a (25MHz) = $\frac{25*10^{6}}{3.5959*10^{10}}(0.1504)^{-1.9}$ = 5.0834×10^{-3}.

Sound velocity u_c was measured by ultrasonic thickness gauge to be 1062$\frac{m}{s}$

The values of the specific heat $C_p\ (t_f)$ is calculated at the frequencies of 5 and 25MHz using equation (4.4.1) as:

$C_p\ (t_f)$ (5MHz) = 2817.07$\frac{J}{Kg.deg}$

$C_p\ (t_f)$ (25MHz) = 1698.01$\frac{J}{Kg.deg}$

The dynamic scaling theory also described the scaling function F(ω*) as a function of reduced frequency ω* at various frequencies theoretically as:

$$F(\omega^*) = (1+\omega^{*-0.5})^{-2} \qquad (4.4.5)$$

The experimental data (Abdelraziq, 2015 to be published) of the ratio of the absorption coefficient at the critical concentration and temperature T $\alpha(x_c,T)$ to the absorption coefficient at the critical concentration and critical temperature $\alpha(x_c,T_c)$ are fitted along with the theoretical curve. The ratio $\frac{\alpha(x_c,T)}{\alpha(x_c,T_c)}$ is calculated at three values of the reduced frequencies and are given in Table (4.7)

Table (4.7): *Values of $\frac{\alpha(x_c,T)}{\alpha(x_c,T_c)}$ at three different frequencies 5, 10 and 25MHz for the critical mixture methanol - cyclohexane

f (MHz)	**ω***	$\frac{\alpha(x_c,T)}{\alpha(x_c,T_c)}$
5MHz	76.0301	0.8211
	7.0349	0.6737
	3.9379	0.6316
	2.5264	0.5684
	1.7634	0.5053
10MHz	152.0602	0.8532
	14.0698	0.7521
	7.8758	0.6761
	5.0528	0.6422
	3.5268	0.5734
25MHz	380.1504	0.8936
	35.1744	0.8532
	19.6895	0.7660
	12.6321	0.7234
	8.8170	0.6596

*: These experimental data are taken from (Abdelraziq, 2015 to be published).

The experimental data of the $\frac{\alpha(x_c,T)}{\alpha(x_c,T_c)}$ of the binary mixture methanol – cyclohexane are presented in Fig. (4.14) as a function of the reduced frequency along with the theoretical fit of the scaling function F(ω*).

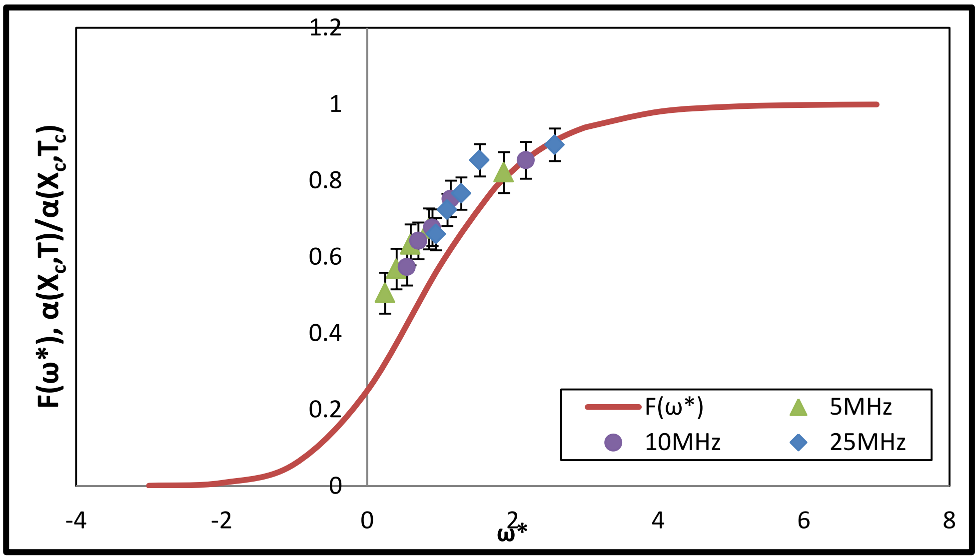

Fig. (4.14): The experimental values of $\frac{\alpha(x_c,T)}{\alpha(x_c,T_c)}$ along with the theoretical scaling function as a function of the reduced frequency.

4.5 Diffusion Coefficient Calculation:

The diffusion coefficient D_o is calculated using the relation below:

$$\omega_0 = 2D_o\xi_0^{-2} \tag{4.4.6}$$

This equation was suggested by (Kawasaki, 1970) and (Ferrell, 1989). At the critical temperature D_o is calculated to be $1.89 \times 10^{-5}\,\frac{\mathrm{cm}^2}{\mathrm{s}}$

Chapter Five

Discussion:

Our experimental results of the dynamic viscosity showed an anomaly at the critical temperature and the critical concentration. The critical temperature is 45.2^{o}C and the critical concentration is 30% by weight of methanol. The results showed a good agreement with Jacobs's experimental result, the critical concentration was found to be 29% by weight of methanol and T_c = 45.1^{o}C (Jacobs, 1986). The results were also in a good agreement with Behrends groups' measurements, the critical concentration was found to be 27.5% by weight of methanol while T_c = 45.7^{o}C (Behrends *et al*, 2003). Our experimental results are also in a good agreement with Fast and Yun. Their values of critical concentration and critical temperature were found to be 28.9% by weight of methanol and 45.9^{o}C respectively (Fast and Yun, 1988).

The specific heat at the critical temperature and concentration $C_{pc}$of the critical mixture methanol – cyclohexane was calculated using the two scale factor universality to be $C_{pc} = 94.24\frac{J}{K.Kg}$ and it showed a good agreement with Kopelman teams' value of $C_{pc} = 95.4\frac{J}{K.Kg}$ (Kopelman *et al*, 1984). The specific heat of the critical binary liquid mixture according to the dynamic scaling theory is a frequency dependent parameter and expresses the lagging in the internal degree of freedom and energy dissipation (Bhattacharjee and Ferrell, 1981).

The density of the critical mixture methanol – cyclohexane was measured to be $769.5\frac{kg}{m^3}$.

The adiabatic coupling constant g for the critical mixture was to be -0.29.The value was less than one which is in a good agreement with Behrends teams' value of g which is $|0.21|$ (Behrends *et al*, 2003). The difference between our value and Behrends value is due the difficulty in determination of the isobaric thermal expansion coefficient. Our value of the isobaric thermal expansion coefficient α_p is $7.00 \times 10^{-3}\ {}^{o}C^{-1}$ while Behrends value was $1.28 \times 10^{-3}\ {}^{o}C^{-1}$ (Behrends *et al*, 2003). The difference between our value of the isobaric thermal expansion coefficient α_p and Behrends's value is may be of different values of critical concentration, critical temperature, noncritical dynamic shear viscosity and critical density. Since the adiabatic coupling constant gives a notation about the coupling between the critical density fluctuation and sound propagation (Bhattacharjee and Ferrell, 1981; Iwanowski, 2007; Bhattacharjee *et al*, 2010). The g depends on pressure, temperature and isobaric thermal expansion coefficient.

The value of the adiabatic coupling constant g for alcohol – alkane systems is considered small compared to the value of g = 1.3 for ethylammonium nitrate – n-octanol and g = 2.1 for isobutyric acid – water. These discrepancies are due to the difference in the values of the critical temperature , critical and background isobaric thermal expansion coefficients $(\alpha_{pc}, \alpha_{pb})$ and because of the difference in the magnitude of $\frac{dT_c}{dP}$ and α_p.

The negative sign of the value of g indicates that the phase separation near the critical point is induced by a sudden decrease in the pressure (Abdelraziq, 1999).

The results of the absorption coefficients were plotted versus the temperature of two frequencies 5 and 25MHz. The temperature of the half of the maximum value of the absorption coefficients per the square of the frequency was determined for each frequency. The values were 51^{o}C for 5MHz and 52^{o}C for 25MHz and the reduced temperature for these values was calculated in order to calculate the dimensionless constant a. The values of a are 6.8772×10^{-3} at 5MHz and 5.0834×10^{-3} at 25MHz. The reason that the data of the ultrasonic absorption coefficients at various frequencies were fitted with temperature but not concentration is that Bhattacharjee and Ferrell theory based on the temperature fluctuation resulting from the adiabatic compression and expansion of the mixture and so the critical behavior takes place only through the fluctuation in ΔT (Bhattacharjee and Ferrell, 1981).

The results of ultrasonic attenuation showed a linear behavior when $\frac{\alpha}{f^2}$ is plotted versus $f^{-1.06}$. The linear relation of the plotted data is in a good agreement with the dynamic scaling theory which predicts this behavior (Bhattacharjee and Ferrell, 1981). The slope of the plotted data of $\frac{\alpha}{f^2}$ versus $f^{-1.06}$ is 1.8452×10^{-7} $\mathrm{cm}^{-1}\mathrm{s}^{0.94}$ and the intercept is 5.5668×10^{-15} $\mathrm{cm}^{-1}\mathrm{s}^{2}$ represents the background absorption coefficient. The value $\frac{\alpha}{\alpha_c}$ rises monotonically as a function of the reduced frequency as it approaches to the critical point. The experimental data of $\frac{\alpha}{\alpha_c}$ as a function of the reduced frequency was compared to the theoretical relation $F(\omega^*) = (1+ \omega^{*-0.5})^{-2}$ (Bhattacharjee and Ferrell, 1981). It is found that the experimental results of $\frac{\alpha}{\alpha_c}$ are in a good agreement with the theoretical assumption by Ferrell and Bhattacharjee (Bhattacharjee and Ferrell, 1981). Compared to other theories, like the mode coupling theories, the experimental results of the dynamic scaling theory fit with the theoretical hypothesis better than mode coupling theories.

The characteristic temperature frequency ω_o was calculated and it is found to be $3.5959 \times 10^{10} s^{-1}$. The value of $\omega_o$according to the dynamic scaling theory is calculated when the energy decay rate of a fluctuation is at ξ^{-1} (Bhattacharjee and Ferrell, 1981).

The diffusion coefficient D was calculated to be $1.89 \times 10^{-5} \frac{cm^2}{s}$

The results of the different properties that have been calculated or measured for the binary liquid mixture methanol – cyclohexane compared with results from literature review are presented in Table (5.1).

Table (5.1): Ultrasonic attenuation results in this work and previous studies.

The measured and calculated value	Our results	Other work
x_c*	30%	29.0% (a) 27.5% (b) 28.9% (c)
T_c*	45.2^oC	45.1^oC (a) 45.7^oC (b) 45.9^oC (c)
C_{pc}**	$94.24\frac{J}{K.Kg}$	$95.4\frac{J}{K.Kg}$ (d)
g**	- 0.29(1st method)	$\lvert 0.21 \rvert$ (b)
α_p**	$7.00\times 10^{-3}\ {}^oC^{-1}$	$1.28\times 10^{-3}\ {}^oC^{-1}$ (b)
α_{pc}**	$3.797 \times 10^{-4}\ {}^oC^{-1}$	–
α_{pb}**	$6.2401 \times 10^{-3}\ {}^oC^{-1}$	–
ρ_c*	$0.7695\frac{gm}{cm^3}$	–
η_o*	0.83cP	–
D_o**	$1.89 \times 10^{-5}\ \frac{cm^2}{s}$	–
u_c	$1062\frac{m}{s}$	–

(a): (Jacobs, 1986), (b): (Behrendes *et al*, 2003), (c): (Fast and Yun, 1988), (d): (Kopelman *et al*, 1984), *: measured value, **: calculated value.

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جامعة النجاح الوطنية
كلية الدراسات العليا

الازدواج الأدياباتيكي الثابت للخليط السائل الثنائي الميثانول والهكسان الحلقي

إعداد
سجى غازي عمر

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

2014

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أ.د. عصام عبد الرازق

الملخص

في هذه الدراسة تم قياس اللزوجة للمخلوط الثنائي ميثانول سايكلوهكسان باستخدام جهاز قياس اللزوجة الرقمي. تم ملاحظة ظاهرة شذوذ اللزوجة لهذا الخليط عند درجة الحرارة الحرجة ($T_c = 45.2\ ^{o}C$) وعند التركيز الحرج بنسبة 30% من الوزن من الميثانول و تم حساب الحرارة النوعية للخليط. تم تطبيق نظرية التوسع الديناميكي لفيريل و باتاشارجي على البيانات لمعامل الامتصاص فوق الصوتي على ترددات مختلفة. ولقد تم ملاحظة العلاقة الخطية بين $\frac{\alpha_c}{f^2}$ و $f^{-1.06}$. ولقد تم حساب ثابت الزدواج الأدياباتيكي للخليط وكذلك معامل التمدد الحراري عند ثبات الضغط للخليط الثنائي الحرج ميثانول – سايكلوهكسان و معامل الانتشار. ولقد رسمت العلاقة بين $\frac{\alpha}{\alpha_c}$ و التردد وتم مقارنتها مع القيم النظرية ووجد بان هناك توافق جيد بين القيم العملية والنظرية للخليط الثنائي الميثانول – سايكلوهكسان.