An-Najah National University
Faculty of Graduate Studies

Modification of the Kawasaki's Analytic Function in Binary Liquid Mixtures

By

Rowaida Mahmoud Eisa Sadeq

Supervisor
Prof. Issam Rashid Abdelraziq

Co-Supervisor
Prof. Mohammed Abu-Jafar

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This thesis was defended successfully on 10/ 04/ 2019 and approved by:

Defense Committee Members

Signature

1. **Prof. Issam Rashid Abdelraziq / Supervisor** ....
2. **Prof. Mohammed Abu-Jafar / Co-Supervisor** ....
3. **Prof. Imad Ahmad Barghouthi/ External Examiner** ....
4. **Prof. Sharif Musameh/ Internal Examiner** ....
5. **Prof. Mohammed El-Saeed/ Internal Examiner** ....

Dedication

I dedicate this project to Almighty Allah my creator. He has been the source of my strength throughout my life. I also dedicate this work to my beloved parents, who have been my source of inspiration and gave me strength when I thought of giving up, who continually provide their moral, spiritual, emotional, and financial support. To my husband who has encouraged me all the way, and whose encouragement has made sure that I give it my all to finish that which I have started. To my children Tala, Lamar and to my twin Amr and Mohammad. To my brothers, sisters, relatives, mentors, friends. Lastly, I dedicate this thesis to everyone who loves science.

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I must express my gratitude to my parents, sibling and to my husband providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without them. Thanks for all your encouragement!

الإقرار

انا الموقع ادناه مقدم الرسالة التي تحمل العنوان:

Modification of the Kawasaki's Analytic Function in Binary Liquid Mixtures

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ACN	pure acetonitrile
FA	Formamide
gm	Gram
K°	Kelvin
ω^*, Ω	the reduced frequency
GHz	Giga Hertz
Db	Decibel
mgm	Milligram
$f(\omega^*)$	the scaling function
H	the critical amplitude
$u(\omega)$	the velocity of sound wave
αf^{-2}	the experimental data of sound absorption, which is a function of frequency and temperature; is the fluctuation absorption, related to the processes in the mixture, when approaching the critical temperature T_c
$\alpha_{reg} f^{-2}$	the regular absorption, related to the structural features of the tested mixtures without fluctuations
$\alpha_{fl} f^{-2}$	the critical ultrasonic attenuation absorption coefficient fluctuation at critical concentration and temperature T related to the processes in the mixture, when approaching the critical temperature
$\alpha_c f^{-2}$	the critical term of ultrasonic attenuation absorption coefficient at critical temperature T_c and critical composition
τ_1	the dispersive area relaxation time
A_1	the relaxation area amplitude
m, n, s	Indexes
$F(\omega *)$	the scaling function introduced
ω_D	the characteristic relaxation frequency of concentration fluctuations
α_t	the critical exponent of the isochoric heat capacity
n	the critical exponent of the correlation length characterizing its dependence on temperature
Z	the dynamic critical exponent
$c_p(t_f)$	the specific heat at a characteristic reduced temperature t_f.
a	dimensionless scaling factor of order unity
ω_0	characteristic temperature dependent relaxation rate
g	adiabatic coupling constant

C_{pc}	The critical amplitude for the specific heat at constant pressure of binary mixture at critical concentration
C_{pb}	the background specific heat
ρ_c	The density at critical temperature and concentration
t	the reduced temperature
α_P	the isobaric thermal expansion coefficient
α_{pc}	the critical thermal expansion coefficient
α_{pb}	the background thermal expansion coefficient
$F(\omega^*)$	the theoretical scaling function
ω	the angular frequency
ω_D	characteristic temperature-dependent relaxation rate
D	the mass diffusion coefficient
ξ	the correlation length
ξ_0	the critical amplitude of the correlation length
μ	the dynamic shear viscosity
x_μ, ν	are the critical exponent
μ_0	the noncritical part of the dynamic shear viscosity
D_0	the diffusion coefficient
$\omega^*_{1/2}$	the half attenuation frequency
α_λ	the ultrasonic attenuation absorption coefficient per wavelength at critical concentration
q	the wave number
K_B	the Boltzmann's constant
γ	the critical exponent
$K(y)$	the analytic function
γ_0	the ratio of heat capacities
$\frac{dT_c}{dP}$	is the slope line of the critical line of consolute points as a function of pressure
d	a dimensionless parameter

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Abstract

The temperature dependence of the ultrasonic attenuation absorption coefficient at critical composition and above critical temperature T_c for the binary mixture nitroethane-isooctane at 5, 7, 10, 15, 21, and 25 MHz frequencies (f) is investigated. In addition, the linear relation of the ultrasonic attenuation absorption coefficient at critical point $(\alpha_c)/f^2$ versus $f^{-1.06}$ showed an excellent agreement with the dynamic scaling theory of Ferrell and Bhattacharjee. The experimental values of $\left(\frac{\alpha f^{-2}}{\alpha_c f^{-2}}\right)$ for nitroethane-isooctane binary mixture are plotted as a function of reduced frequency ω^* and it showed a good agreement with the theoretical scaling function $F(\omega^*)$. Furthermore, Fixmen, Kawasaki, Hornowski, Mistura, and Chapan function failed to explain the experimental behavior of the binary liquid mixtures at critical composition and above critical temperature according to mode coupling theories. In this thesis we corrected the analytic function of Fixmen's, Kawasaki's, Hornowski's, Mistura's, and Chapan's theories was corrected in order to get an agreement with the experimental behavior of the binary liquid mixtures at critical composition and above the critical temperature.

Chapter One

Introduction

A sound wave is a longitudinal, mechanical pressure wave; regions of high pressure are compressions and low-pressure regions are rarefactions.

Binary liquid mixtures are a system consists of two pure liquid substances, which have a limited solubility of each one in the other [1]. The point at which binary system behaves the same homogenous phase under the same condition, pressure, specific heat, viscosity, and thermal conductivity is the critical point of binary mixture. This point illustrates the boundary between areas of homogeneous and heterogeneous behavior in phase diagrams for binary mixtures [2]. Binary liquid mixtures has many applications in engineering, biological and industrial processes present a wide choice of solutions with suitable properties. Ultrasonic can be a useful tool for gaining qualitative information of some physical parameters in these binary liquid mixtures [3].

1.1 Literature Review

Theoretical and experimental studies of critical binary mixtures, near the critical separation temperature T_c are a topic of lively scientific debates [4–8], they cover a wide range of unique and universal properties of such systems and their practical use [9-11]. A multiple of thermodynamic properties have been calculated by studying the attenuation of ultrasonic waves through liquids [5,12-19].

Densities and ultrasonic speeds of pure acetonitrile (ACN) l-butanol, formamide (FA) and those of eighteen binary mixtures of ACN with l-butanol and FA were measured at 30gm. and 15 K°[20]. Also, isentropic compressibility, intermolecular free length, relative association, acoustic impedance, molar sound speed, excess isentropic compressibility, excess intermolecular free length, excess volume, deviation in ultrasonic speed and excess acoustic impedance were calculated using different theories and relations from the experimental data [20].

The critical behavior of sound propagation through absorption or dispersion for different binary liquid mixtures at critical composition and above critical temperature have been studied by scientists and researchers [21-50]. The most important models that discussed the behavior of sound waves propagation are the renormalization group theory by kroll and Ruhland [50], the dynamic scaling theory by Ferrell and Bhattacharjee [16] and a package of mode- coupling theory by Fixmen [51], Kawasaki and Shiwa [52], Chapan [53], Mistura [54], and Hornowski [55]. These theories failed to describe the experimental data over a wide range of the reduced frequency ω^*. These theories are based on the view that understanding the fluctuations that occur in those binary mixture rather than focus on microscopic aspects [56-58]. Kawasaki mode-Coupling theory was developed in terms of critical behavior of bulk viscosity. Kawasaki studied theoretically the sound attenuation and dispersion using the extended mode-mode coupling theory [52].

Hornowski and Labowski [55] applied the modified version of the mode coupling theory for the acoustic anomaly based on the critical behavior of a relaxing complex heat capacity.

Guixiang Ma and his group investigated the thermal properties and thermal reliability of stearic acid-n-butyramide and stearic acid-n-octanamide binary eutectic mixtures, as phase change materials for low temperature solar heat energy storage. The solid-liquid phase diagrams of two binary systems were established and the eutectic compositions of binary mixtures and corresponding thermal properties were verified: (1) stearic acid-nbutyramide, the eutectic composition is 0.551 ± 0.005 mol fraction stearic acid and (2) stearic acid-noctanamide,the eutectic composition is 0.589 ± 0.005 mol fraction stearic acid. The mixture has a good thermal stability after 100 melt-freeze cycles. As novel phase change materials for solar heat applications, the studied eutectic mixtures have attractive thermal performance and great utility [59].

Abdelraziq [40-48] developed the modified mode-coupling theory by Hornowski [55] to describe the critical attenuation of the binary system of Aniline and cyclohexane. He found that there is poor agreement between this modification and experimental data above 10 MHz of reduced frequency. Latifa and his group showed that current theories cannot describe the velocity $u(\omega)$ and absorption of hypersound in critical mixtures at frequencies above 4 GHz [37]. A lot of the thermodynamic properties of the solution process, including the Gibbs free energy, enthalpy, and entropy were calculated for different binary liquid mixtures at different temperatures [60- 67].

Volumetric and ultrasonic properties of ionic liquids, speed of sound, the density values were used to calculate excess molar volume, whereas speed of sound results have been used to calculate deviation in isentropic compressibility. The excess properties and spectroscopic data have been analyzed in terms of the effect of temperature and the change of the anion of ionic liquid [68, 71].

The ultrasonic absorption and velocity $u(\omega)$measurements were studied as a function of temperature and frequency for different binary mixtures, the viscosity and many thermodynamic properties were measured [20-62]. Densities and viscosities of different ionic liquids were measured by Dongren Cai et al, [72] at different temperatures as a function of molality (or mass fraction). The isobaric thermal expansion coefficient, molecular volume, standard molar entropy, and lattice energy of the pure ionic liquid were obtained based on the density data of pure ionic liquid [72]. The apparent molar volume, infinite dilution apparent molar expansibility, and energy barrier were calculated from the experimental data [72].

The shear behavior of binary mixtures via a two-dimensional discrete element method was investigated by Gong and Liu [73]. The effect of the coarse particle content on the peak shear strength of mixtures is investigated for different contact-type friction coefficients. The inter-particles structures are examined when the binary mixtures become coarse-particle-supported structures [73]. The excess heat capacities were calculated from the measured molar heat capacities data of the binary as well as ternary mixtures at different temperatures by Sharma et al [74].

1.2. Objectives and Motivations

The aim of the present investigation is to compare the experimentally determined ultrasonic attenuation absorption coefficient in binary liquid mixtures with Kawasaki mode coupling theory. In order to have an agreement between the theoretical and experimental data for the ultrasonic attenuation absorption coefficient in binary liquid mixtures, it is necessary to predict a new suitable formula for Kawasaki analytic function.

1.3. Experimental technique

Measurements of absorption and velocity $u(\omega)$ are made using Matec pulse – echo technique. The following Matec equipment was used: a radio frequency gated amplifier model 515, which is a plug-in unit of Matec gating modulator model 5100, a doubled turned –amplifier model 252, a broadband receiver model 605 and model 666 pulse-comparator, which generates a pulse of radio frequency energy, which can be precisely controlled in amplitude in steps of 0.1dB up to a total of 61dB. The sample was prepared by the weight using an Ohaus 1600 series balance and Sartorius scale which has a precision of 0.05 mg. The purification of chemicals was 99.9%. The absorption and velocity $u(\omega)$ of sound were measured above the critical temperature and shaken several times to ensure complete mixing. The test cell was also heated above the critical temperature before the sample was added. The pulse comparator was used to measure the height of the echoes viewed on the oscilloscope. For a given number of interference peaks, the displacement of the reflector, which leads to the wavelength, is measured and used with the frequency to determine the velocity of sound $u(\omega)$ in liquid.

1.4. Dissertation Organization

The thesis is divided of five chapters. Chapter one is the introduction which presents a review of ultrasonic studies in different liquid mixtures. Chapter two discusses the mode-coupling theories of Fixmen, Kawasaki and Shiwa, Mistura, Chapan, and Hornowski which was applied for analyzing the ultrasonic information. Methodology of the work is shown in chapter three, while the measured data and the results are shown in chapter four. Conclusions are presented in chapter five.

Chapter two

Theory

Ultrasonic attenuation is the decay rate of the sound wave as it propagates through material. There are many theoretical models that have discussed the ultrasonic attenuation through binary liquid mixtures at the critical points. Kroll D. M. and Ruhaland J. M. [50] have studied a model for sound propagation in critical binary mixtures using renormalization-group theory and expansion methods. The basis of this theory is to describe the behavior of ultrasonic propagation in the existence of consolute point to calculate the bulk viscosity. The only significant contribution to the bulk viscosity comes directly from order-parameter fluctuations, and renormalization-group theory. New scaling relations for the critical attenuation and dispersion are obtained, the critical ultrasonic attenuation absorption coefficient per wavelength was written as the following [50]:

$$\frac{\alpha_\lambda(crit)}{u^2(\omega)} = \pi H \, Im \, F(\omega^*) \qquad (1)$$

Where $\alpha_\lambda(crit)$ is the critical ultrasonic attenuation absorption coefficient per wavelength, $F(\omega^*)$ is the scaling function, H is the critical amplitude, $u(\omega)$ is the velocity of sound wave, and ω^* is the reduced frequency. Scientists used renormalization group theory [50] in order to explain the critical behavior of binary mixture.

Taking into account the theory of dynamic scaling theory [16, 73-75], the ultrasonic attenuation absorption coefficient αf^{-2} is the sum of regular and fluctuation components [76]:

$$\alpha f^{-2} = \alpha_{reg} f^{-2} + \alpha_{fl} f^{-2} \tag{2}$$

where αf^{-2} is the experimental data of sound absorption, which is a function of frequency and temperature; $\alpha_{reg} f^{-2}$ is the regular absorption, related to the structural features of the tested mixtures without fluctuations; $\alpha_{fl} f^{-2}$ is the fluctuation absorption, related to the processes in the mixture, when approaching the critical temperature T_c.

Regular absorption connected with the changes in the molecular structure of the mixture by conformation processes, formation of associates, dimers or complexes, is described by the formula with one relaxation area for binary mixtures in the test frequency range [77, 78].

$$(\alpha f^{-2})_{reg} = \left[\frac{A_1}{(1+(\omega\tau_1)^{2s})^{\frac{m+n}{2s}}}\right] \tag{3}$$

where $\omega = 2\pi f$ is the angular frequency; τ_1 is the dispersive area relaxation time; A_1 is the relaxation area amplitude; indeces m, n, s equal (0,1], introduced by Hill [77] to take account of collective processes, determine the ultrasonic attenuation absorption coefficient frequency dependence. For the test mixture m=n=s=1.

Fluctuation component analysis was performed using Ferrel and Bhattacharjee [16] theory of relaxing heat capacity

$$(\alpha_{fl} f^{-2}) = (\alpha_c f^{-2}) F(\omega *) \tag{4}$$

Where $\alpha_c f^{-2}$ is the ultrasonic attenuation absorption coefficient t at critical point, and $F(\omega *)$ is the scaling function introduced by the authors [16]; $\omega *$ is the scaled frequency $\omega * = \frac{\omega}{\omega_D} = \frac{2\pi f}{\omega_0 t^{z\nu}}$, ω_D is the characteristic relaxation frequency of concentration fluctuations, ν is the critical exponent of the correlation length characterizing its dependence on temperature; z is the dynamic critical exponent.

Dynamic scaling theory in binary mixture is based on the frequency dependent specific heat concept. The total critical ultrasonic attenuation absorption coefficient at the critical temperature and concentration in the dynamic scaling theory by Ferrell and Bhattacharjee can be expressed as [16]:

$$(\alpha_c f^{-2}) = S . f^{-\left[1+\frac{\alpha_t}{z\nu}\right]} + \alpha_b f^{-2} \tag{5}$$

where $\alpha_c f^{-2}$ - is the ultrasonic attenuation absorption coefficient at critical point, α_t is the critical exponent of the isochoric heat capacity (a subindex t is used not to take the exponent for the absorption coefficient α); S is the amplitude of frequency dependence of the singular part of the ultrasonic attenuation absorption coefficient α_t=0.11 and $z\nu$ = 1.9 are the critical exponents [40].

The S value is given by Ferrell and Bhattacharjee [16].

$$S = [\frac{\{\pi C_{pc} g^2 u(\omega) \alpha_t\}}{\{2 z\nu T_c C_p^2(t_f)\}}][\frac{a\omega_0}{2\pi}]^{\frac{\alpha_t}{z\nu}} \qquad (6)$$

Where $c_p(t_f)$ is the specific heat at a characteristic reduced temperature t_f, a $= (\frac{\omega}{\omega_0})^t f^{-z\nu}$ is dimensionless scaling factor of order unity, ω_0 is characteristic temperature dependent relaxation rate, g is adiabatic coupling constant, u(ω) is the adiabatic sound velocity at T_c. The critical amplitude for the specific heat at constant pressure of binary mixture at critical concentration, C_{pc} is represented by [78,79]:

$$C_p = c_{pc} t^{-\alpha_t} + c_{pb} \qquad (7)$$

Here C_{pb} is the background specific heat thermal expansion coefficient. The adiabatic coupling constant g is presented to verify the subdivision in attenuation spectra into the critical contribution and the sophisticated background contribution. The adiabatic coupling constant g depends on pressure, temperature and isobaric thermal expansion coefficient. The g factor may be negative or positive. The negative sign of g factor indicates that the phase separation near the critical point is induced by a sudden decrease in the pressure. The positive sign for the g factor indicates that the phase separation near the critical point is induced by a sudden increase of the pressure. The adiabatic coupling constant is given by [79]:

$$g = \rho_c C_p \left[\frac{dT_c}{dP} - \frac{T\alpha_p}{\rho_{c_p}} \right] \cong \frac{C_{pb}\alpha_{pc}T_c}{C_{pc}} - \alpha_{pb} T \qquad (8)$$

where ρ_c is the density at critical temperature and concentration; the reduced temperature t is represented by: t $= \frac{T-T_c}{T_c}$; α_p is the isobaric thermal expansion coefficient which is given:

$$\alpha_p = \alpha_{pc} t^{-\alpha_t} + \alpha_{pb} \qquad (9)$$

Note that α_p is the isobaric thermal expansion coefficient, α_{pc} and α_{pb} are the critical background parts of the thermal expansion coefficient, α_{pc} is the critical thermal expansion coefficient and α_{Pb} is the background thermal expansion coefficient. $C_p(t_f)$ is the specific heat at a characteristic reduced temperature t_f. The critical term of the absorption can be represented as a function of the dimensionless reduce frequency Ω or ω* which is [40, 16]:

$$\left(\frac{\alpha_{fl} f^{-2}}{\alpha_c f^{-2}} \right) = F(\omega *) \qquad (10)$$

$\alpha_{fl} f^{-2}$ is the critical absorption at critical concentration and temperature T, while $\alpha_c f^{-2}$ is the critical term at critical T_c and critical composition. F(ω *) is the theoretical scaling function.

where ω is the angular frequency, ω_D is a characteristic temperature-dependent relaxation rate that can be approximated by Stokes- Einstein expression: $\omega_D = 2D\xi^{-2}$ where D is the mass diffusion coefficient and [54]:

$$\omega_D = \frac{K_B T}{3\pi\mu\xi^3} = \frac{K_B T_C}{3\pi\mu_0\xi_0^3} t^{zv} = \omega_0 t^{zv} \qquad (11)$$

Using the relationships $\omega_0 = 2D_0\xi_0^{-2}$, for the correlation length $\xi = \xi_0 t^{-\nu}$ and the dynamic shear viscosity $\mu = \mu_0 t^{-x_\mu \nu}$. While ξ_0 is the critical amplitude of the correlation length, x_μ, ν are the critical exponent [40] ($\nu = 0.64$, $-x_\mu \nu = 0.037$); μ_0 is the noncritical part of the dynamic shear viscosity whereas D_0 is the diffusion coefficient.

Taking into account theoretical expression for crossover function [16].

$$F(\omega *) = \frac{1}{\left[1+0.414(\frac{\omega*_{1/2}}{\omega*})n\right]^2} \tag{12}$$

Where $\omega*_{1/2}$ is the reduced half attenuation frequency.

the final formula for ultrasonic attenuation absorption coefficient fluctuation looks like

$$\left(\alpha_{fl} f^{-2}\right) = S.f^{-\left[1+\frac{\alpha_t}{z\nu}\right]}\left[1 + 0.414\left(2\pi f.\omega *_{1/2}\, \tau_{fl}\right)^{-n}\right]^{-2} \tag{13}$$

allowing the finding of relaxation time of concentration fluctuation in the test solution according to the experimental data of the ultrasonic attenuation absorption coefficient for different temperatures near the critical point.

The final model discussed in this research is the mode coupling theories developed by Fixmen [51], Kawasaki and Shiwa [52, 53], Mistura and Chapan [54], and Hornowski [55].

The mode-coupling theories by Fixmen, Mistura, Chapan, Kawasaki and Shiwa lead to the same general expression for the ultrasonic attenuation absorption coefficient per wavelength α_λ at critical concentration [51-55]:

$$\frac{\alpha_\lambda}{u^2(\omega)} = \pi A(T) F(\omega *) \tag{14}$$

where A(T) is the critical amplitude which is different for each theory, $u(\omega^*)$ is the velocity $u(\omega)$ of sound, and F(ω *) is the scaling function. The general form of the scaling function is given by equation (2) [51-55]:

$$F(\omega^*) = \int \{ \left[\frac{y^2\, dy}{(1+y^2)^2} \right] [\frac{\omega * K(y)}{K(y)^2 + \omega *^2}] \} \tag{15}$$

Where y = qξ , q is the wave number and $\xi = \xi_0 t^{-\nu}$ is the correlation length, while ξ_0 is the critical amplitude of the correlation length, the reduced temperature t, T_c is the critical temperature of the binary mixture,

K(y) is the analytic function. In Fixman model the analytic function K(y) is given by [51]:

$$K(y) = y^2 [1 + y^2] \tag{16}$$

While Kawasaki’s analytic function is given by[52]:

$$K(y) = \frac{3}{4} \left[1 + y^2 + (y^3 - \frac{1}{y}) tan^{-1}(y) \right] [1.055^a + \{0.93 + 0.29 \log_{10}(y)\}^a]^{\frac{1}{a}} \tag{17}$$

With fitting exponent a = 13.

The Mistura’s and Chapan’s analytic function is [54].

$$K(y) = \frac{3}{4} \left[1 + y^2 + (y^3 - \frac{1}{y}) tan^{-1}(y) \right] \tag{18}$$

The critical amplitudes A(T) of the binary mixture in the mode-coupling theories are given as follows:

Fixman's and Kawasaki's critical amplitudes $A_F(T)$ and $A_K(T)$ are given by [44, 51, 52]:

$$A_F(T) = A_K(T) = \left[\frac{K_B\,(\gamma_0 - 1)\,\nu^2}{\pi\rho u C_{Pb}\xi_0^3}\right]t^{-\alpha} \tag{19}$$

Where K_B is Boltzman's constant, ρ is the density of the mixture, C_{Pb} is background heat capacity at constant pressure, $\gamma_0 = \frac{C_P}{C_V}$ is the ratio of heat capacities, ξ_0 is the correlation length. The form of Mistura's critical amplitude is given by [54, 44]:

$$A_M(T) = A_F(T)\,[\gamma_0 - 1]^{-2}[1 - 0.5\eta]^2 \tag{20}$$

Chaban's form $A_C(T)$ is given by[54, 44]:

$$A_C(T) = A_F(T)\left[1 - \left(\frac{\rho C_{Pb}}{\alpha_{Pb}}\right)\left(\frac{dT_C}{dP}\right)\right]^2 \tag{21}$$

α_{Pb} is the background amplitude of the thermal expansion, $\frac{dT_C}{dP}$ is the slope of the critical line of consolute points as a function of pressure, and η, ν, α are critical exponents which equal to 0.04, 0.62, 0.11, respectively [44].

Hornowski and Labowski [55] applied the modified version of the mode coupling theory for the acoustic anomaly based on the critical behavior of a relaxing complex heat capacity. The general expression for the critical amplitude $A_H(T)$ is given by:

$$A_H(T) = A_K(T)[1 - 0.5\eta]^2 f(d) \tag{22}$$

Where η is a critical exponent = 0.04, d is a dimensionless parameter $d = \left[\frac{\rho\, C_{Vb}}{T\alpha_{Pb}}\right]\left[\frac{dT_c}{dP}\right]$ and the function $f(d)$ is given by:

$$f(d) = |(\gamma_0 d - 1)^2 - 2d\gamma_0[d - (\gamma_0 - 1)^{-1}]| \tag{23}$$

C_{Vb} is background heat capacity coefficient and α_{Pb} is background thermal expansion coefficient.

Chapter Three

Methodology

The binary liquid mixture nitroethan-isooctane system has a chemical form of $C_2H_5NO_2$ - C_8H_{18}, it has a critical temperature of Tc = 31.5℃ at critical composition of 0.50356 by weight of isooctane.

3.1 The characteristics of the binary mixture components

The binary mixture used in this research consists of the compounds nitro ethane and isooctane, nitro Ethan is a colorless oily liquid with a pleasant odor. Flash point of 27.78C˚. Decomposes above 350F˚. Density is 1.052 g / cm^3. Vapors are much heavier than air. It is insoluble in water. Vapor may irritate skin, eyes and mucous membranes, produces toxic oxides of nitrogen during combustion. It is used as a propellant and as a solvent, nitroethane is a nitroalkane that is ethane substituted by a nitro group. It is a tautomer of an aci-nitroethane. The molecular formula of nitroethan is $C_2H_5NO_2$ or $CH_3CH_2NO_2$ and the molecular weight is 75.067 gm\mol. Isooctan or 2,2,4-Trimethylpentane is a clear colorless liquid with a petroleum-like odor. Less dense than water and insoluble in water. Vapors are heavier than air. Isooctane is an alkane that consists of pentane bearing two methyl substituents at position 2 and a single methyl substituent at position 4. It has a role as a fuel additive, a non-polar solvent and a nephrotoxin. It is an alkane and a volatile organic compound, the molecular formula of isooctan is $CH_3C\ (CH_3)_2\ CH_2CH\ (CH_3)_2$ or C_8H_{18}

with molecular weight of 114.232 gm\ mol, the density of isooctane is 0.69 g/cm^3 (20 °C).

3.2 Statistical analysis

The statistical program MATLAB is used to analyze and plot data for ultrasonic attenuation absorption coefficient for nitroethan and isooctan binary mixture.

Chapter Four

Results and Discussion

The binary mixture Nitroethane and Isooctane has a critical temperature of Tc = 31.5℃ at critical composition of 0.50356 by weight of isooctane. The ultrasonic attenuation absorption coefficient α_λ at different temperatures and at 5, 7, 10, 15, 21 and 25 MHz frequencies for the critical binary mixture of Nitroethane and Isooctane were measured using the Matec pulse-echo technique that generates pulses through the temperature-controlled test cell.

Fig. 1 shows the ultrasonic attenuation absorption coefficient (αf^{-2}) versus temperature at different frequencies.

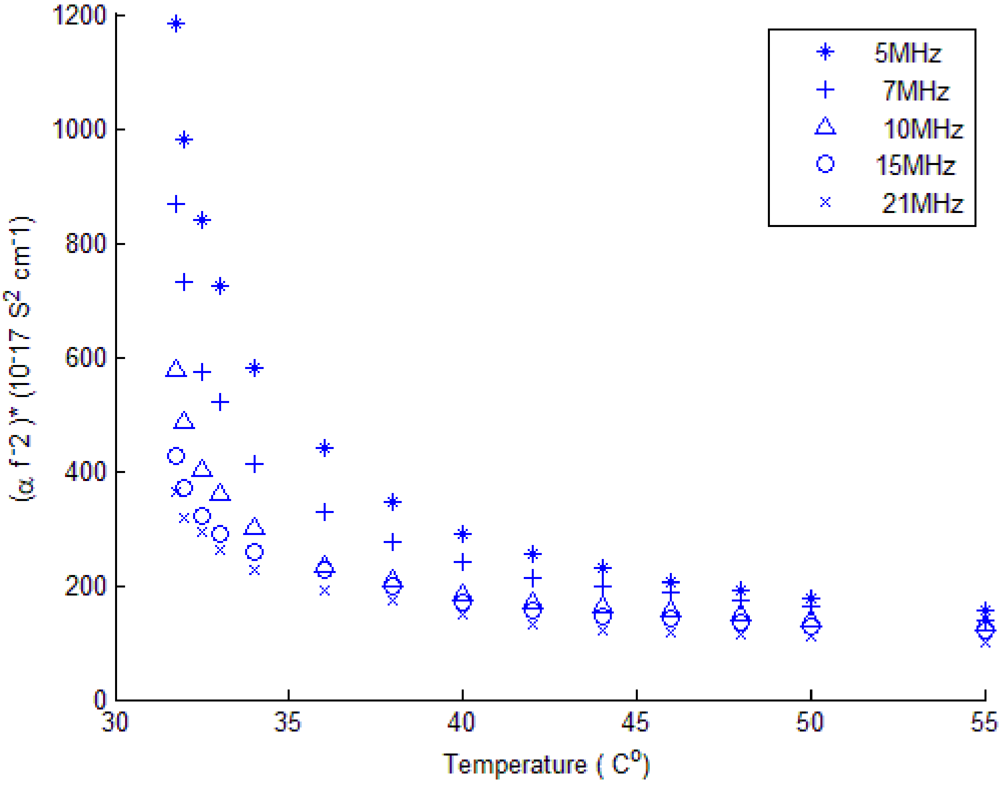


Figure1: Temperature dependence of αf^{-2} for the critical binary mixture of nitroethane- isooctane.

Firstly, the regular part of the ultrasonic attenuation absorption coefficient $(\alpha f^{-2})_{reg}$ was calculated. It was made for the processing of experimental data given on Fig.1 using formula (3) for non-critical temperature range. Experimental data for the temperature range $\Delta T = T - T_c \geq 2K^{\circ}$, where we observed anomalous absorption, was processed with the help of Mathcad.

The received results of processing equation (3) parameters dependent on the temperature for all tested mixture concentrations were approximated in the temperature range with anomalous sound absorption.

This created a possibility of receiving numeric values of ultrasonic attenuation absorption coefficient fluctuation part$(\alpha f^{-2})_{fl}$, according to equation (2), having experimental data on the sound absorption and calculated values of regular absorption component.

The dynamic scaling theory of Ferrell and Bhattacharjee shows that $\frac{\alpha_{fl} f^{-2}}{\alpha_c f^{-2}}$ should be a function of the reduced frequency ω*, and should be scaled with the scaling function *F*(ω*). According to the theory $(\alpha_c f^{-2})$ versus $f^{-1.06}$ must give a straight line at the critical temperature and composition. A linear relation between the ultrasonic attenuation absorption coefficient $(\alpha_c f^{-2})$ versus $f^{-1.06}$, at Tc = 31.5 ℃ and at critical composition 0.50356 by weight of isooctane for the critical binary mixture of nitroethane-isooctane, is shown in Fig. 2.

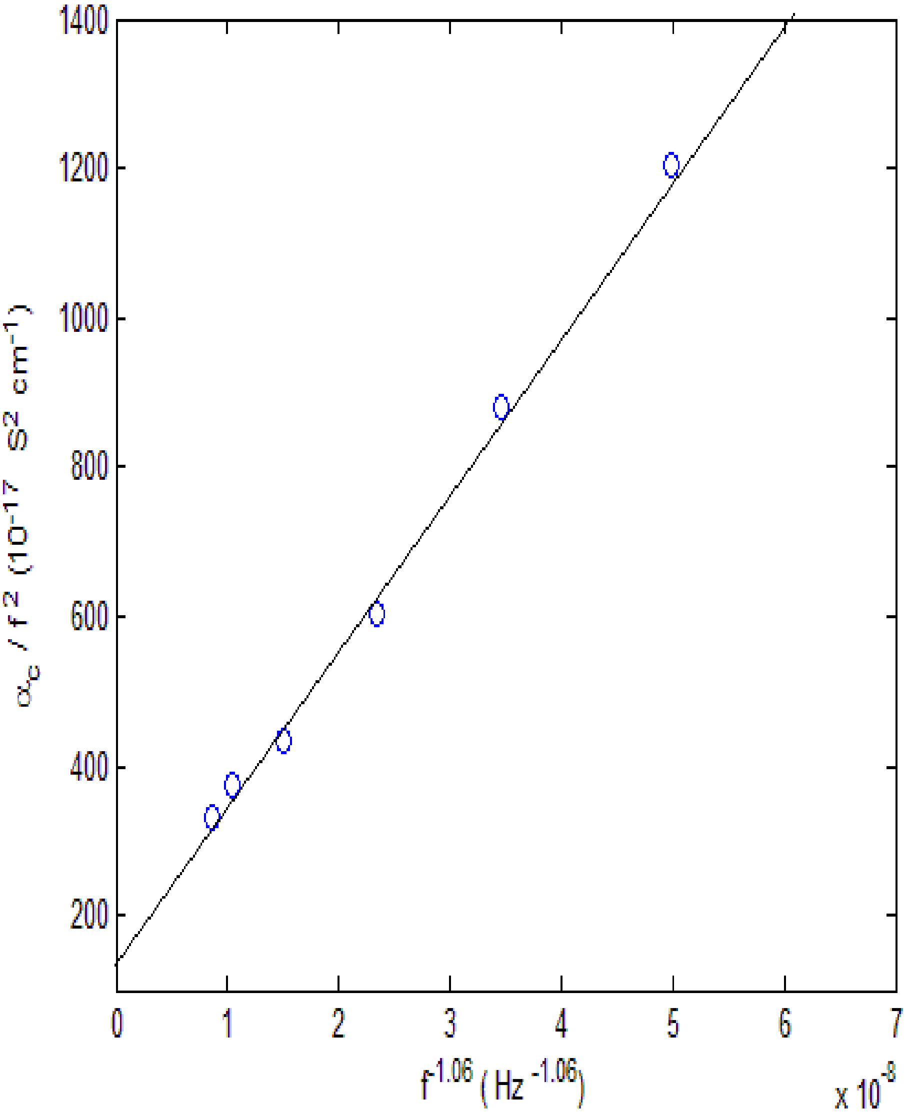


Figure 2: The absorption ($\alpha_c f^{-2}$) versus $f^{-1.06}$ at T_c and critical mixture for nitroethane- isooctane.

The slope S = 2.13×10^{-7}cm^{-1}s$^{0.94}$ and the intercept of 134.63×10^{-17}cm^{-1}s^{2} represents the frequency independent background term of $(\alpha_c f^{-2})$. The data forms a straight line as shown by Ferrell and Bhattacharjee theory.

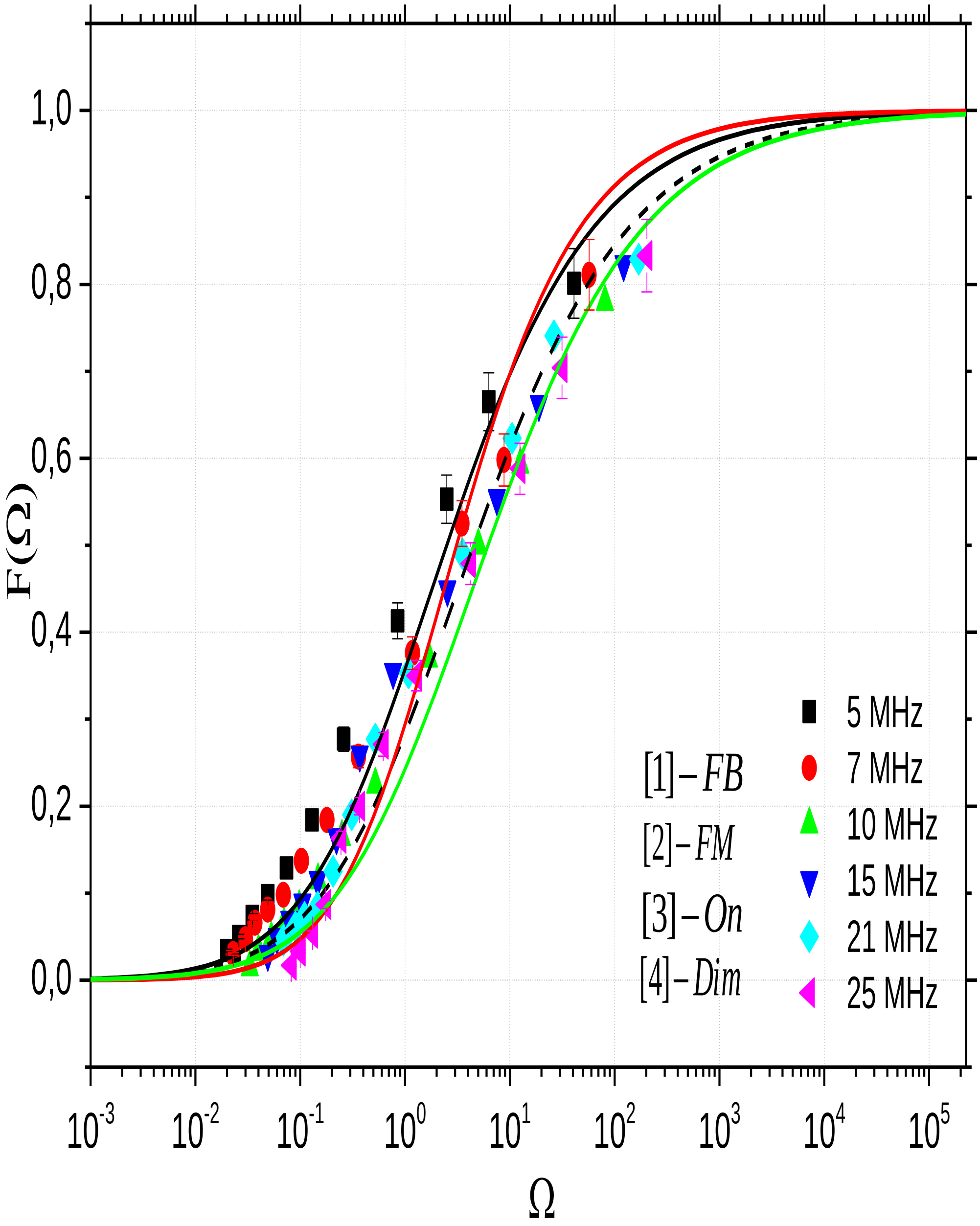


Figure 3: The plot of $\frac{(\alpha_{fl} f^{-2})}{(\alpha_c f^{-2})} = F(\Omega)$ versus the reduced frequency Ω or ω*.

Processing of experimentally received scaling function by equation (13) within the bounds of Ferrel and Bhattacharjee heat capacity relaxing theory, allowed to find the parameters values of equation (13): $n = 0.53 \pm 0.03$ and $\Omega_{1\backslash 2} = 2.5 \pm 0.05$ [56] (in Fig. 3). The received values should be compared with results of other works: $n = 0.5$ and $\Omega_{1\backslash 2} = 2.1$ [63]; $n =$

0.63 and $\Omega_{1\backslash 2}$ = 3.1[57]; n = 0.5 and $\Omega_{1\backslash 2}$ = 6.2 [58], corresponding curves [1], [2] and [3] respectively.

The experimental data of $\frac{(\alpha_{fl} f^{-2})}{(\alpha_c f^{-2})}$ as function of the reduced frequency is in good agreement with the theoretical scaling function as assumed by Ferrell and Bhattacharjee [16].

The temperature independent relaxation rate for the critical binary mixture of nitroethane-isooctane is ω_0=6.51945×1010 Hz and the diffusion coefficient D_0 equals 1.90903×10^{-9} m^2/s. The adiabatic coupling constant (g) was calculated by Hornowski *et al* [55, 56] was found to be 0.356 [55, 66]. In our work the experimental adiabatic coupling constant g = 0.24829±0.00111 and the theoretical adiabatic coupling constant g = 0.3582, were in good agreement with Hornowski team [55, 66]. The results of different properties that have been calculated or measured for the critical binary mixture of nitroethane-isooctane were compared with results from literature review presented in Table 1.

Table (1): The values of different physical properties that have been measured or calculated for the binary mixture of nitro ethane and isooctane, which are found in this work and other works.

Quantity	Measured	Calculated	References
S($cm^{-1}S^{0.94}$) at 35℃	2.13×10^{-7}	$(2.7761 \pm 0.0702372) \times 10^{-7}$	
g at 35℃	0.3582	0.24829±0.00111	0.356[19]
$\omega_0\,(Hz)$		6.51945×10^{10}	
D_0(m^2/S)		1.90903×10^{-9}	
$\frac{dT_c}{dP}\,(K.Pa^{-1})$			$(2.6\pm0.5)\times10^{-8}$ (20)
ξ_0		2.42	
ρ_c(Kg/m^3)		813	
C_{Pc} (J/Kg.K)		214.31	
C_{Pb}(J/Kg.K)			1750 [19]

Analysis of nitroethane-isooctane critical binary mixture ultrasonic attenuation absorption coefficient temperature and frequency dependences properties as the sum of regular and fluctuation parts, for the first time allowed the making of a surface (Fig.4) as a function of concentrations fluctuations relaxation time τ_{fl} according to the formula 24 which derived from equations 2, 3 and 14:

$$\alpha f^{-2} = S.\left[1 + 0.414\,.\left(2\pi f.\Omega_{1\backslash 2}\tau_{fl}\right)^{-2}\right]^{-2}.f^{-\left[1+\frac{\alpha_t}{z\nu}\right]} + \Sigma_{i=1}^{2}\left[\frac{A_i}{[1+(\omega\tau_i)^{2s}]^{\frac{m+n}{2s}}}\right] + B \quad (24)$$

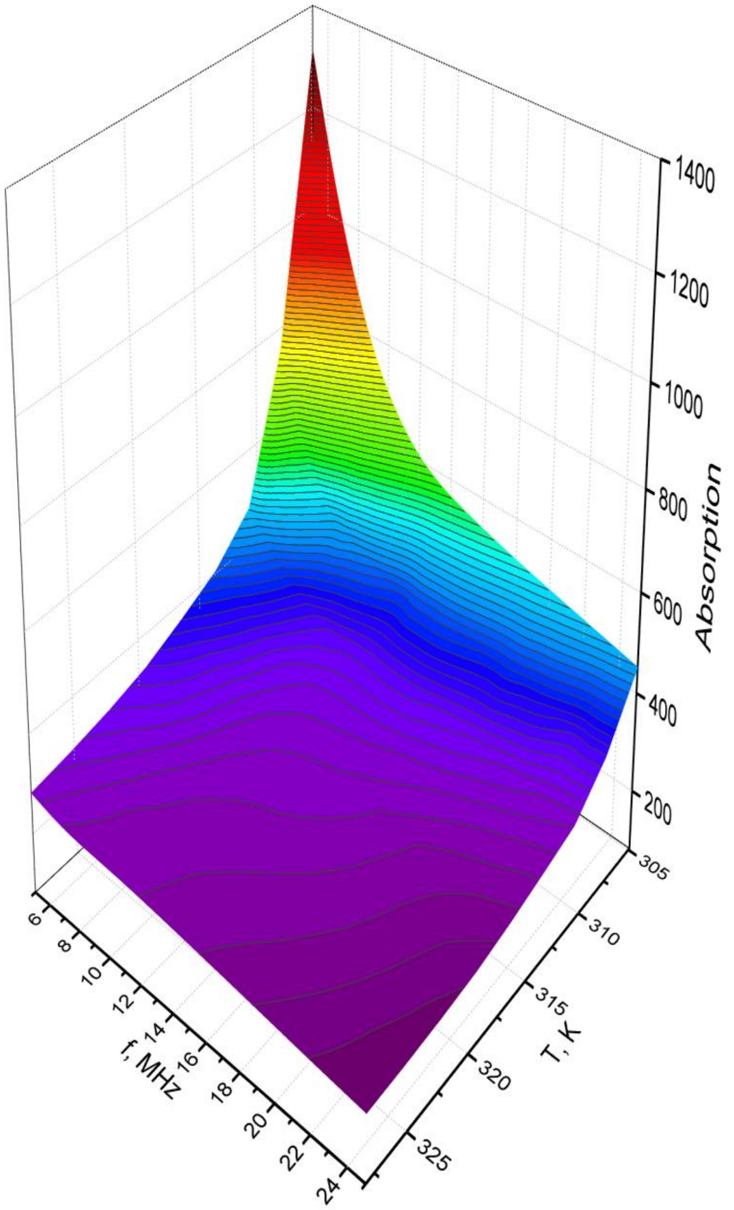


Figure 4: The surface of ultrasonic attenuation absorption coefficient as a function of temperature and frequency.

From equation (15) we can expect that the experimental values of F(ω*) depend on the amplitude A(T) and other same constants for specific binary mixture, from comparison between equations (19, 20, 21, and 22) we conclude that the experimental values for Fixmen and Kawasaki are the same so the modification will be the same for the two models.

Figures 5, 6, 7, 8, and 9 represent plots of experimental absorption attenuation values of F(ω*) versus the reduced frequency ω* for Nitroethane and Isooctane binary mixture at 5, 7, 10, 15, 21 and 25 MHz frequencies of Fixmen's, Kawasaki's, Hornowskie's, Mistura's, and Chapan's expressions respectively, along with the theoretical scaling integral F(ω*).

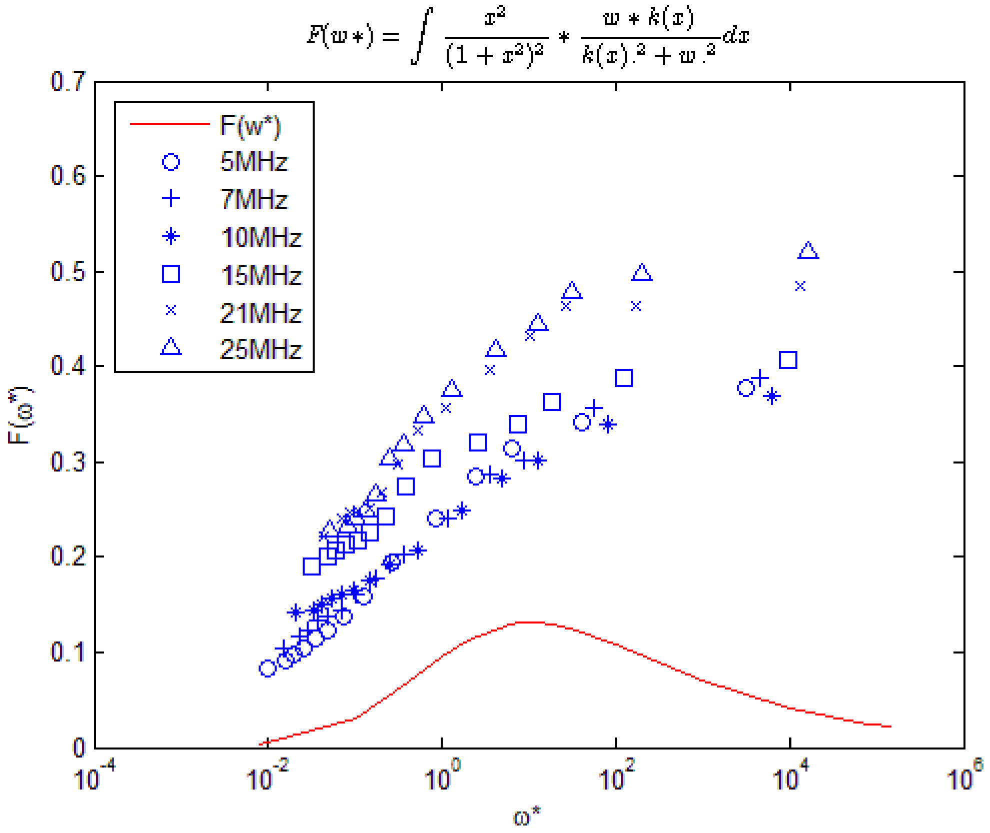
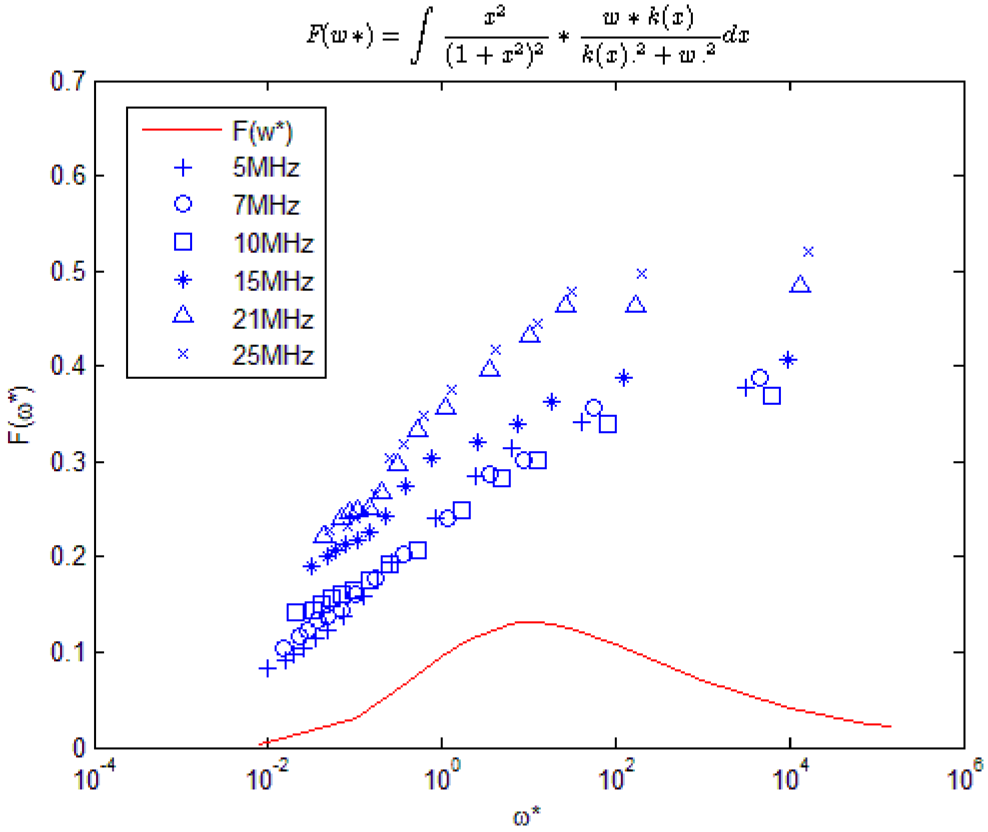


Figure 5: The experimental absorption values of $\frac{\alpha_\lambda}{\pi u^2(\omega)A(T)}$ versus the reduced frequency ω* for Nitroethane and Isooctane binary mixture at 5, 7, 10, 15, 21 and 25 MHz frequencies according to Fixmen theory along with the theoretical scaling integral F(ω*).



$$F(w*) = \int \frac{x^2}{(1+x^2)^2} * \frac{w*k(x)}{k(x).^2 + w.^2} dx$$

Figure 6: The experimental absorption values of $F(\omega *) = \frac{\alpha_\lambda}{\pi u^2(\omega)A(T)}$ versus the reduced frequency ω* for Nitroethane and Isooctane binary mixture at 5, 7, 10, 15, 21 and 25 MHz frequencies according to Kawasaki and Shiwa theory along with the theoretical scaling integral F(ω*).

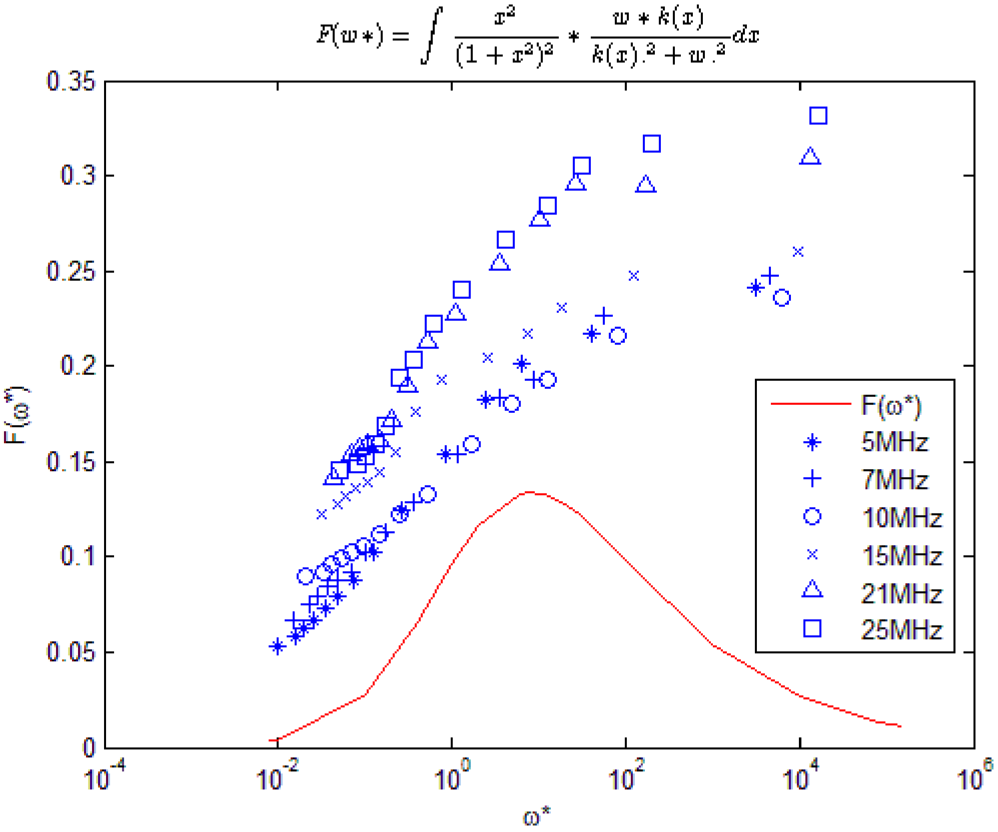


Figure 7: The experimental absorption values of $F(\omega *) = \frac{\alpha_\lambda}{\pi u^2(\omega)A(T)}$ versus the reduced frequency ω* for Nitroethane and Isooctane binary mixture at 5, 7, 10, 15, 21 and 25 MHz frequencies according to Hornowski and Labowski theory along with the theoretical scaling integral F(ω*).

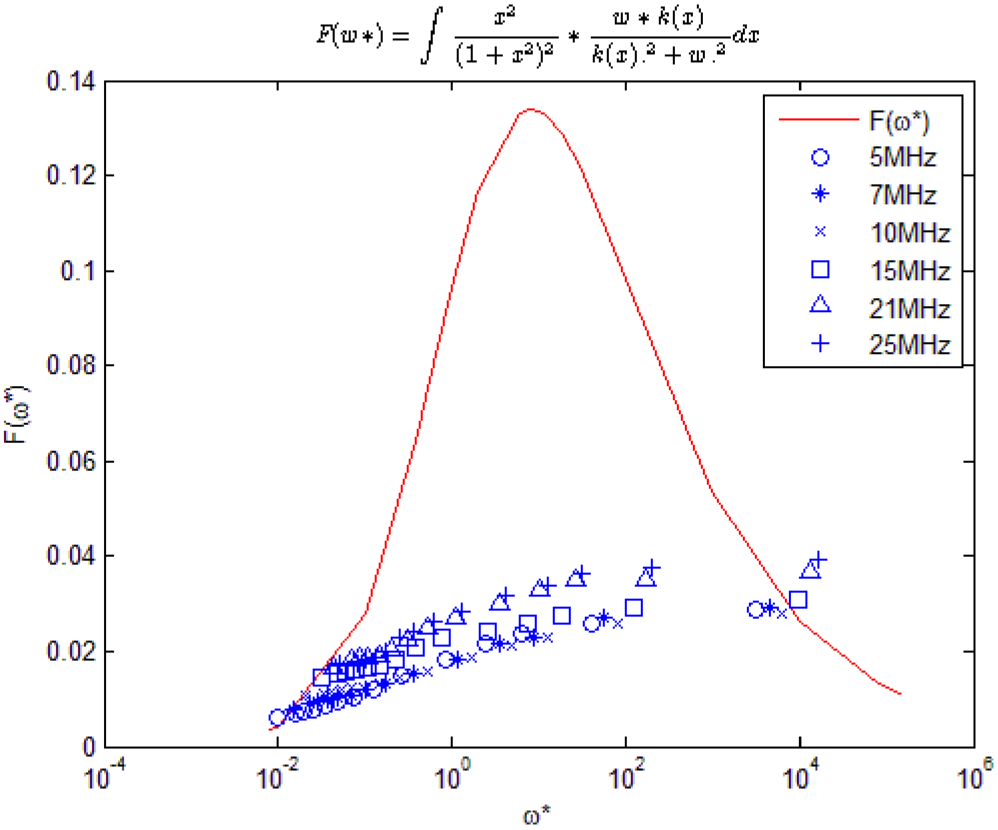


Figure 8: The experimental absorption values of $F(\omega *) = \frac{\alpha_\lambda}{\pi u^2(\omega)A(T)}$ versus the reduced frequency ω* for Nitroethane and Isooctane binary mixture at 5, 7, 10, 15, 21 and 25 MHz frequencies according to Mistura theory along with the theoretical scaling integral F(ω*).

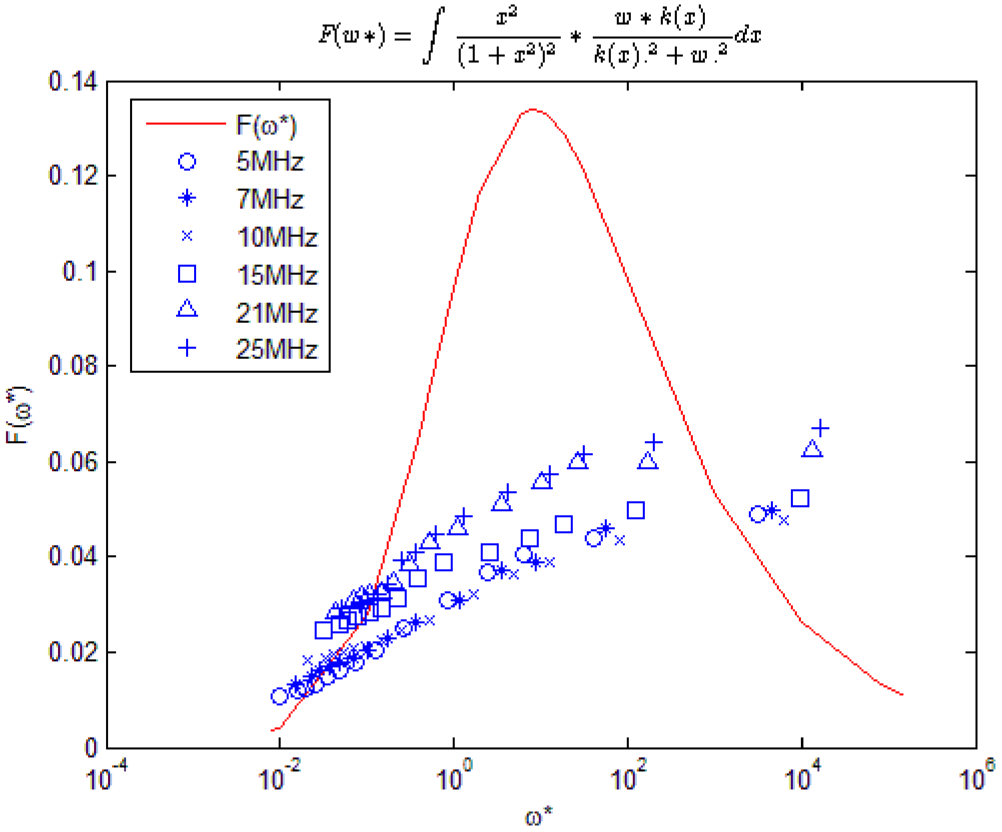


Figure 9: The experimental absorption values of $F(\omega *) = \frac{\alpha_\lambda}{\pi u^2(\omega)A(T)}$ versus the reduced frequency ω* for Nitroethane and Isooctane binary mixture at 5, 7, 10, 15, 21 and 25 MHz frequencies according to Chapan theory along with the theoretical scaling integral F(ω*).

The provided figures (5-9) illustrate that there is a disagreement between the theoretical and experimental data at different frequencies, because of this disagreement, we focus our efforts in this study to modify the analytic function for the mode-coupling theory in order to have an agreement between theory and the experimental data for F(ω*) at different frequencies and temperatures for the five mode coupling theories. The analytic function K(y) affects in the form of the scaling function F(ω*) as shown in equation (15). The final modified form of the analytic function $k_m(y,\omega^*)$is given by the relation:

$$k_m(y,\omega^*) = \frac{\omega^* + \omega^* \times \sqrt[2]{1 - 4\left[\left(\frac{y^2+y}{1+y^2}\right) \times \left[-0.1762 \times \omega^{*^{-0.225}} + 0.5428\right]\right]^2}}{2\left[\left[\frac{y^2+y}{1+y^2}\right] \times \left[-0.1762 \times \omega^{*^{-0.225}} + 0.5428\right]\right]} \qquad (25)$$

Fixmen, Kawasaki, Hornowski, Mistura, and Chapan modification analytic function is applied to the binary mixture Nitroethane-Isooctane. The modified analytic function depends on the correlation length ($y = q\xi$) and the reduced frequency $\omega^* = \frac{2\pi f}{\frac{k_B T}{3\pi\mu_0\xi_0^3} t^{z\nu}}$ which depends on the correlation length (ξ) and depends also on the shear viscosity μ.

Figures from 10 and 11 predict plots of Fixmen and Kawasaki experimental absorption attenuation values of F(ω*) versus the reduced frequency ω* for Nitroethane and Isooctane binary mixture at 5, 7, 10, 15, 21 and 25 MHz frequencies. The general modification for the analytic function is given in equation (25) along with the theoretical scaling integral F(ω*).

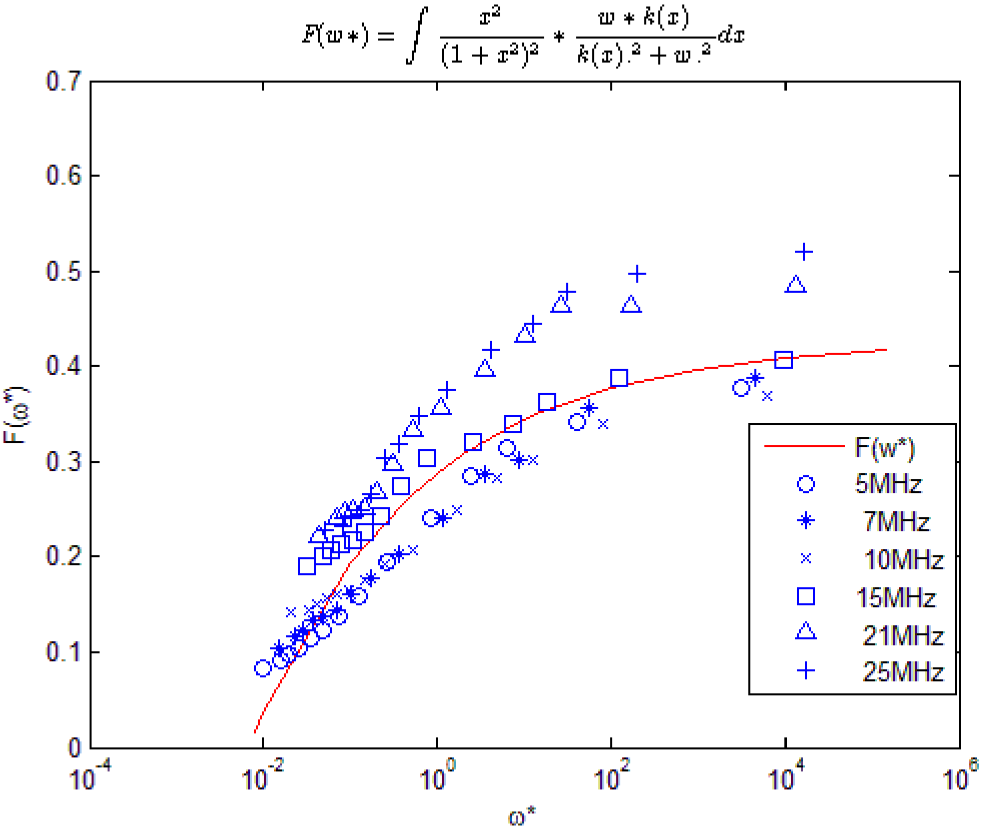


Figure 10: Kawasaki's experimental data of the absorption attenuation coefficient per wavelength α_λ at critical concentration at different frequencies 5, 7, 10, 15, 21 and 25 MHz for the binary mixture Nitroethane-Isooctane versus the reduced frequency ω^* frequencies according to the general modification for the analytic function K(y, ω*)[equation 25].

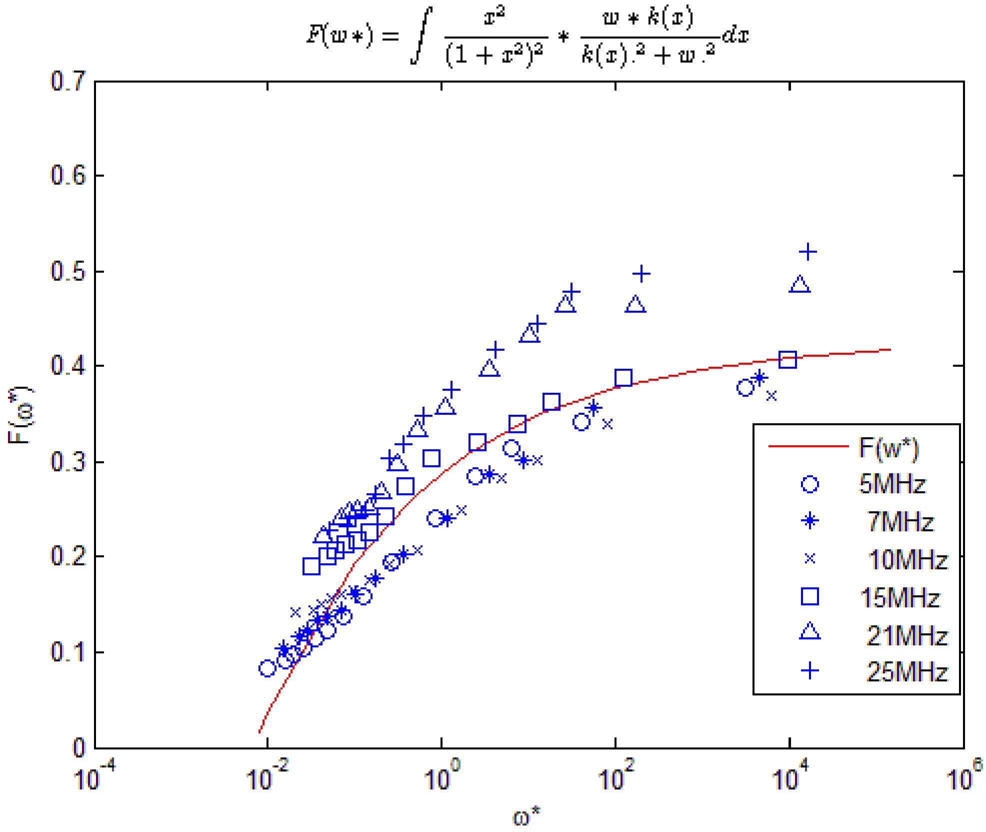


Figure 11: Fixmen's experimental data of the absorption attenuation coefficient per wavelength α_λ at critical concentration at different frequencies 5, 7, 10, 15, 21 and 25 MHz for the binary mixture Nitroethane-Isooctane versus the reduced frequency ω^* according to the general modification for the analytic function K(y, ω*).

Figures 10 and 11 show an excellent agreement for large reduced frequency ω^* between experimental values and theoretical predictions for the general modified analytic function K(y, ω*). The correction of the analytic function K(y, ω*) according to Hornowski theory $k_{mH}(y,\omega^*)$ is given in equation (26):

$$k_{mH}(y,\omega^*) = \frac{\omega^* + \omega^* \times \sqrt[2]{4 - 4\left[\left(\frac{y^2+y}{1+y^2}\right) \times \left[-0.1762 \times \omega^{*\,-0.225} + 0.5428\right]\right]^2}}{2\left[\left[\frac{y^2+y}{1+y^2}\right] \times \left[-0.1762 \times \omega^{*\,-0.225} + 0.5428\right]\right]} \qquad (26)$$

Figure 12 represents plot of Hornowski experimental absorption attenuation values of F(ω*) versus the reduced frequency ω* for

Nitroethane and Isooctane binary mixture at 5, 7, 10, 15, 21 and 25 MHz frequencies, the new general modification for the analytic function is given in equation (26) along with the theoretical scaling integral F(ω*).

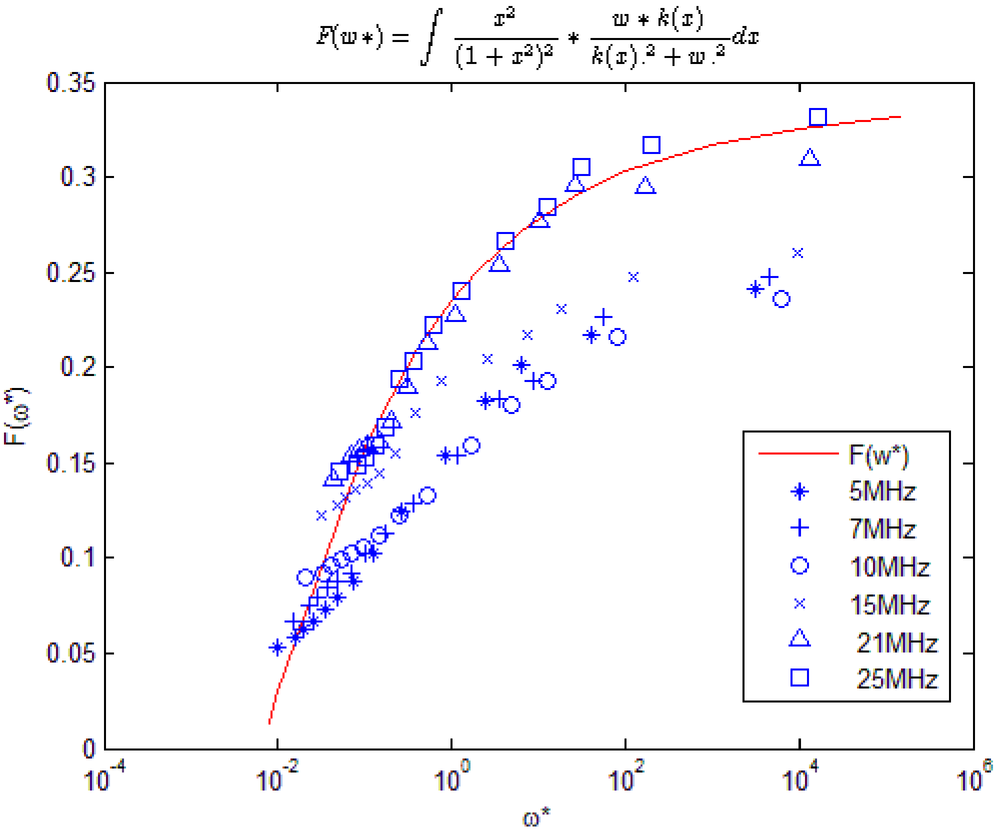


Figure 12: The experimental data of absorption values of F(ω*) = $\frac{\alpha_\lambda}{\pi u^2(\omega)A(T)}$ versus the reduced frequency ω* for Nitroethane and Isooctane binary mixture at 5, 7, 10, 15, 21 and 25 MHz frequencies according to the new modified Hornowski model of $k_{mH}(y,\omega^*)$.

For Mistura theory, the new correction for the modified analytic function $k_{mM}(y,\omega^*)$ is given by equation (27):

$$k_{mM}(y,\omega^*) = \frac{\omega^* + \omega^* \times \sqrt[2]{559-4\left[\left(\frac{y^2+y}{1+y^2}\right)\times\left[-0.1762\times\omega^{*-0.225}+0.5428\right]\right]^2}}{2\left[\left[\frac{y^2+y}{1+y^2}\right]\times\left[-0.1762\times\omega^{*-0.225}+0.5428\right]\right]} \qquad (27)$$

Figure 13 predicts plot of Mistura experimental absorption attenuation values of F(ω*) versus the reduced frequency ω* for Nitroethane and

Isooctane binary mixture at 5, 7, 10, 15, 21 and 25 MHz frequencies, the new general modification for the analytic function $k_{mM}(y,\omega^*)$ is given in equation (27) along with the theoretical scaling integral F(ω*).

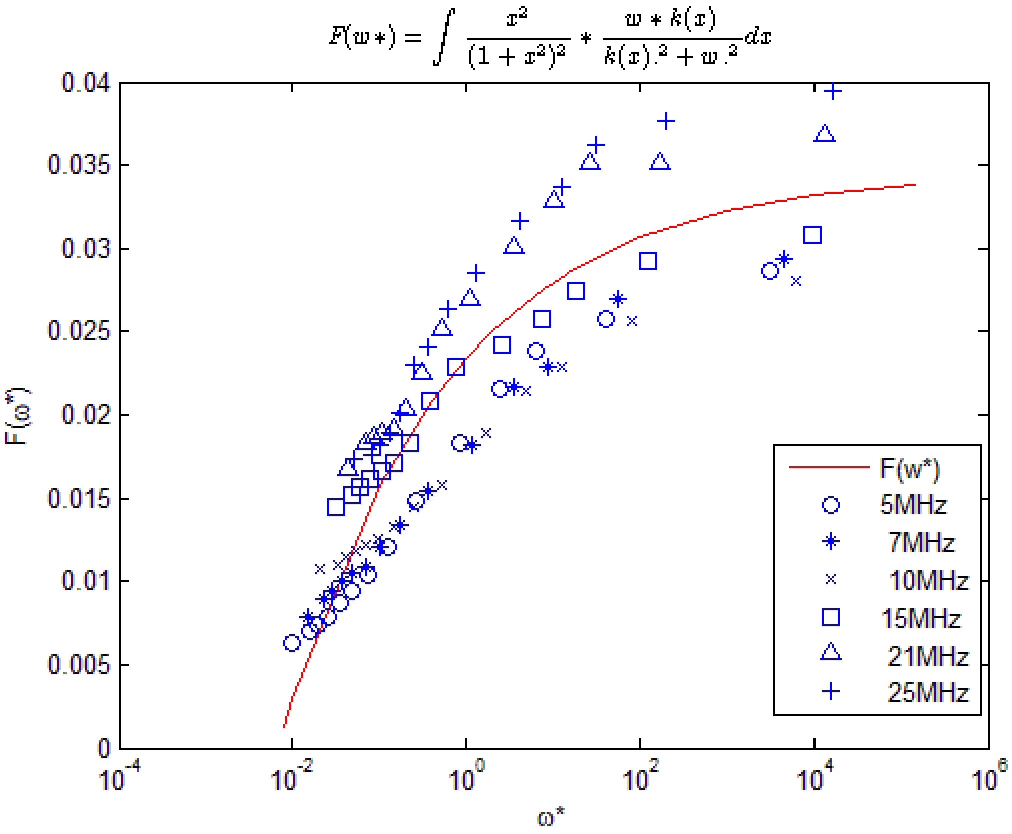


Figure 13: The experimental data of absorption values of F(ω*) = $\frac{\alpha_\lambda}{\pi u^2(\omega)A(T)}$ versus the reduced frequency ω* for Nitroethane and Isooctane binary mixture at 5, 7, 10, 15, 21 and 25 MHz frequencies according to the new modified Mistura model of $k_{mM}(y,\omega^*)$.

Finally, for Chapan theory the new correction for the modified analytic function $k_{mC}(y,\omega^*)$ is given by equation (28):

$$k_{mC}(y,\omega^*) = \frac{\omega^* + \omega^* \times \sqrt[2]{197 - 4\left[\left(\frac{y^2+y}{1+y^2}\right)\times\left[-0.1762\times\omega^{*^{-0.225}}+0.5428\right]\right]^2}}{2\left[\left[\frac{y^2+y}{1+y^2}\right]\times\left[-0.1762\times\omega^{*^{-0.225}}+0.5428\right]\right]} \qquad (28)$$

Figure 14 predicts plot of Chapan experimental absorption attenuation values of F(ω*) versus the reduced frequency ω* for Nitroethane and

Isooctane binary mixture at 5, 7, 10, 15, 21 and 25 MHz frequencies, the new general modification for the analytic function $k_{mC}(y, \omega^*)$ is given in equation (28) along with the theoretical scaling integral F(ω*).

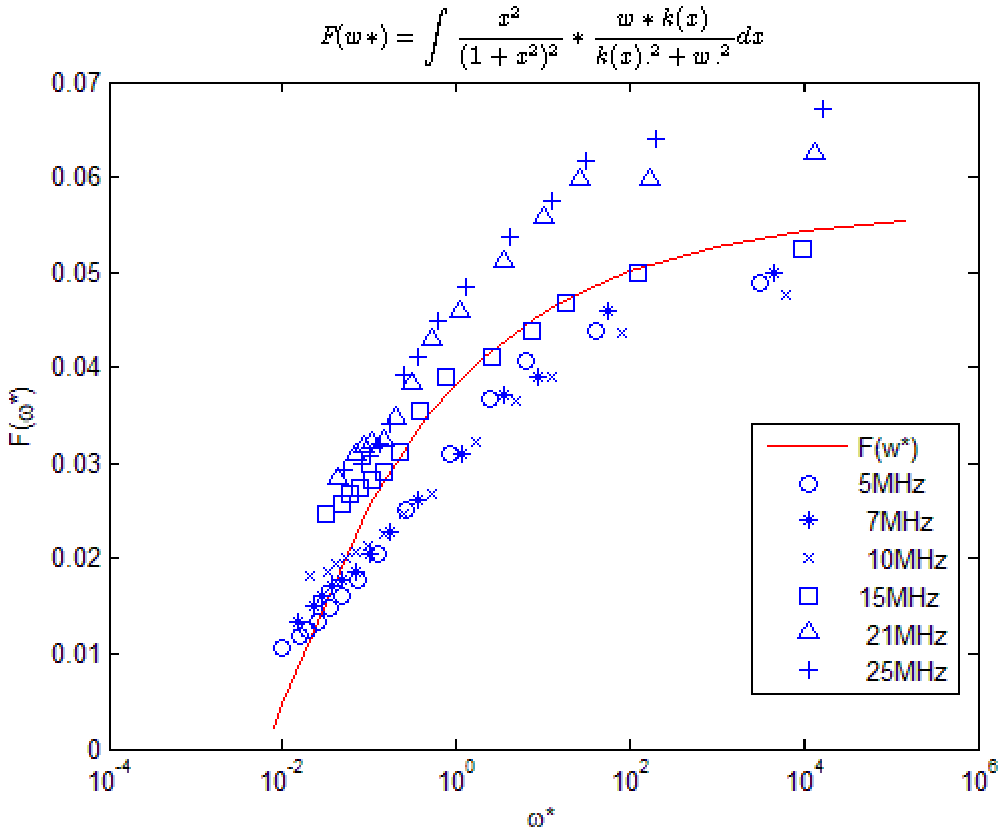


Figure 14: The experimental data of absorption values of F(ω*) = $\frac{\alpha_\lambda}{\pi u^2(\omega)A(T)}$ versus the reduced frequency ω* for Nitroethane and Isooctane binary mixture at 5, 7, 10, 15, 21 and 25 MHz frequencies according to the new modified Chapan model of $k_{mC}(y, \omega^*)$.

Figures 12, 13 and 14 show an excellent agreement for large reduced frequency ω^* between experimental values and theoretical predictions for the modified analytic function.

At the end of this section we conclude from the results we have in all previous five models of mode- coupling theories that we can unite trend for modification of these theories. We modify the analytic function K(y) to $K(y, \omega^*)$, the experimental data for the five theories have the same shape but differ in the vertical amplitude because the experimental data for $F(\omega^*)$ depends on the amplitude $A(t)$ as shown in equation (1), and the amplitude $A(T)$ for Fixmen theory equals with Kawasaki theory and also, the amplitude for Mistura, Chapan and Hornowski theories depends on Fixmen and Kawasaki amplitude as shown in equations (20), (21), and equation (22) in addition to other constant parameters for the same binary liquid mixture, so the result we have for the modification analytic function for Mistura, Hornowski and Chapan have the same general formula but it must differ in vertical amplitude.

Chapter Five

Conclusion

The ultrasonic attenuation absorption coefficient at critical temperature and critical composition for the critical binary mixture nitroethane-isooctane decreases as the temperature increases for all frequencies. The ultrasonic attenuation absorption coefficient for the critical composition and above critical temperature decreases with increasing frequency at different temperatures. The results of $\alpha_c f^{-2}$ versus $f^{-1.06}$ yield a straight line as shown by Ferrell and Bhattacharjee theory. The experimental data of the critical and background parts of the ultrasonic attenuation absorption coefficient as function of the reduced frequency is in a good agreement with the theoretical scaling function as predicted by Ferrell and Bhattacharjee theory. The positive sign for the g factor indicates that the phase separation near the critical point is induced by a sudden increase of pressure.

Mode-coupling theories were used to describe the critical behavior of binary liquid mixtures and above critical point. The analytic function of Fixmen, Kawasaki, Mistura, Hornowski and Chapan theories are not suitable to yield proper scaling function in order to get an agreement with experimental data. The analytic function of Mode-coupling theories K(y) relates to the correlation length $y = q\xi$. The disagreement between theoretical and experimental data for Fixmen, Kawasaki, Mistura, Hornowski and Chapan theories for sound propagation in binary liquid mixture is shown in figures 6 to 10. The modified Kawasaki's, Fixmen's, Mistura’s, Hornowski’s and Chapan’s analytic function depend on the correlation length ξ and on the shear viscosity μ. By Introducing these physical parameters, Fixmen, Kawasaki, Mistura, Hornowski and Chapan theories is improved to describe the critical behavior of binary liquid mixtures above critical temperature and at critical concentration. In order to explain the trend of the experimental data, the modification of the analytic function presents an excellent agreement between theoretical and experimental data for sound propagation in binary liquid mixture.

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جامعة النجاح الوطنية

كلية الدراسات العليا

تعديل الاقتران التحليلي لنظرية كافازاكي في مخاليط السوائل الثنائية

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قدمت هذه الرسالة استكمالا لمتطلبات الحصول على درجة الدكتوراة في الفيزياء بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس – فلسطين

2019

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الملخص

لقد تم استخدام النتائج العملية المقاسة للاضمحلال الصوتي لدراسة نظرية فيكسمان وكافازاكي ومستورا وشبان وهرنوسكي التي تختص بالسوائل ثنائية المخاليط عند النقطة الحرجة. واظهرت النتائج ان النظريات الخمس المذكورة انفا لم تنجح في وصف السلوك الحرج بشكل يتوافق مع النتائج التجريبية خاصة عند الترددات العالية للخليط الثنائي نيتروايثان– ايسواوكتان، تم تعديل الاقتران التحليلي لنظريات فيكسمان وكافازاكي ومستورا وشبان وهرنوسكي واسهم هذا التعديل في تغيير شكل الاقتران الاتزاني ليتوافق مع شكل الاقتران الاتزاني التجريبي.