Modification of the Fixman's AnalyticFunction in Binary Liquid Mixtures

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Abstract

The mode-coupling theory of Fixman failed to explain the experimental behavior of the binary liquid mixtures at critical concentration and above critical temperature. The analytic function of Fixman's theory was modified in order to get an agreement with the experimental behavior of the binary liquid mixtures at critical concentration and above the critical temperature. Ultrasonic absorption and velocity of some binary liquid mixtures were used to test thevalidity of the Modified-Fixman's theory.It is found that the ratio of heat capacities$\gamma_0 = \frac{c_V}{c_p}$(at constant volume and pressure) of the binary liquid mixtures is the term which plays the role to modify the Fixman's theory to get a good agreement with the experimental behavior.

Introduction:

Binary mixture is a system contains two systems that not have a homogenous composition, and become uniform thermodynamic properties after critical point at which binary system behave same homogenous phase under the same condition of temperature, pressure, specific heat, viscosity, and thermal conductivity (C. Greer and R. Hocken, 1975)

The simple fluid systems can be studied by using the ultrasonic pressure amplitude attenuation per wavelength $\alpha_\lambda(\omega)$ or absorption coefficient and the sound velocity $u(\omega)$, mainly when absorption coefficient of ultrasound near critical point is being observed It was found that there is an increase in this absorption and loss of energy from the sound wave to the fluctuations near the critical point (Mistura, 1972; Shiwa, 1977; Garland and Sanchez, 1983).

Several theories studied the critical behavior of binary liquid mixtures. One of these theories is mode coupling theory which was developed by Fixman to describe the absorption and dispersion of sound near critical point of binary mixture (Fixman 1962). Mode-coupling theory developed by Kawasaki in terms of critical behavior of bulk viscosity (Kawasaki, 1970). Mistura focused on the critical behavior of complex specific heat (Mistura, 1972),the second theory byKroll-Ruhland and Onuki which described the propagation of acoustic wave in the vicinity of critical point using the renormalization group theory to determine the bulk viscosity (Kroll and Ruhland, 1981). The third theory byFerrel-Bhattacharjee which developed the dynamic scaling theory for the critical ultrasonic attenuation in a binary liquid mixture (Ferrel and Bhattacharjee, 1981, 1985). Tanaka and Wada showed that the form of critical amplitude of in Kroll-Ruhland is the same as in the case ofFerrel-Bhattacharjee dynamic scaling theory(Tanaka and Wada, 1985). Hornowski and his groupdeveloped the modified version of the mode-coupling

theory for the acoustic anomaly based on the critical behavior of a relaxing complex heat capacity(Hornowski et al, 1989).

In this paper, the mode-coupling theory of Fixmanwill be used to explain the behavior of the experimental data. Correction terms may be added to the theory to be able to explain the trend of the experimental data

Theory

The mode-coupling theories lead to the same general expression for the attenuation per wavelength α_λ at critical concentration (Kawasaki, 1970; Shiwa and Kawasaki, 1981) which is:

$$\frac{a_\lambda}{u^2(\omega)} = \pi A(T) I(\omega^*)$$

(1)

Where;

$u(\check{S})$ is the velocity of sound.

$A(T)$ is the critical amplitude.

$I(\check{S}^*)$ is the scaling function.

However, the expression for critical amplitude $A(T)$ is different for each theory. The scaling function is generalized relaxation function, which is given by (Kawasaki, 1970; Shiwa and Kawasaki, 1981):

$$I(\omega^*) = \int \left[\frac{x^2 dx}{\{1+x^2\}^2}\right]\left[\frac{\omega^* K(x)}{[K(x)^2+\omega^{*2}]}\right]$$

(2)

Where ω^* reduced frequency $\omega^* = \frac{\omega}{\omega_D}$.

ω_D is the characteristic frequency given by

$$\omega_D = 2D_0 \xi_0^{-2} t^{1.93}$$

(3)

Where;

D_0 is the diffusion coefficient (Mistura, 1972; Bhattacharjee and Ferrell, 1981)

ξ_0 is the correlation length.

Near the critical point mass diffusion coefficient satisfies an Stokes-Einestien expression, hence Eq. (10) can be written in the following form:

$$\omega_D = \frac{k_B T}{3\pi\mu\xi^3} = \frac{k_B T}{3\pi\mu_0\xi_0^3} t^{(3+\chi_\mu)\nu}$$

(4)

Where the correlation length and shear viscosity are given by formula (Calmettes, 1977)

$\xi = \xi_0 t^{-\nu}$ and $\mu = \mu_0 t^{\chi_\eta}$

k_B is the boltzmann's constant.

and $t = \frac{T-T_c}{T_c}$ is the reduced temperature, which determines distance from the critical point

on temperature scale.

The formula (11) can be written in the form:

$$\omega_D = \omega_0 t^{zv} \tag{5}$$

Where;

$z = 3 + \chi_\mu$, v and χ_μ are critical exponents with $(zv = 1.93)$

The analytic function $K(y)$ of Kawasaky, Mistura, and Chaban is given by (Garland andSanchez, 1983; Shimakawa, 1960).

$$K(x) = \frac{3}{4}\left[1 + x^2 + \left(x^3 - \frac{1}{x}\right)arctan(x)\right] \tag{6}$$

While the Fixman's analytic function $K(x)$ is given by (Mistura, 1972)

$$K(x) = x^2[1 + x^2] \tag{7}$$

The expressions for 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 (Garland andSanchez, 1983; Roe and Meyer, 1978):

$$A_F(T) = A_K(T) = \left[\frac{K_B(\gamma_0 - 1)v^2}{\pi \rho u \, C_{pb}\xi_0^3}\right]t^{-\alpha} \tag{8}$$

Mistura's form of the critical amplitude is given by (Garland andSanchez, 1983; Shimakawa, 1960).

$$A_M(T) = A_F(T)[\gamma_0 - 1]^{-2}[1 - 0.5\eta]^2 \tag{9}$$

Chaban's form $A_C(T)$ is given by (Fuchs et al, 1998):

$$A_C(T) = A_F(T)[1 - \left(\frac{\rho C_{pb}}{\alpha_{pb}}\right)\left(\frac{dT_c}{dP}\right)]^2 \tag{10}$$

Where;

...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.

α_{pb} is the background amplitude of the thermal expansion.

ξ_0 is the correlation length, $\frac{dT_c}{dP}$ is the slope of the critical line of consolute points as a function of pressure. T_C is the critical temperature of the binary mixture and η, v, α are critical exponents.

Hornowski's modification is based on the critical behavior of a relaxing complex heat capacity. The general expression for the critical amplitude $A_H(T)$ has been derived in terms of the dimensionless parameter (HornowskiandLabowski, 1989)

$$d = \left[\frac{C_{vb}\ \rho}{T\ \alpha_{pb}}\right]\left[\frac{dT_c}{dP}\right] \tag{11}$$

Where C_{vb} is the back ground specific heat coefficient at constant volume

The critical Hornowski's amplitude $A_H (T)$ is given by (HornowskiandLabowski,1989):

$$A_H(T) = A_K(T)[1\text{-}0.5\eta]^2 f(d) \tag{12}$$

Where the function

$$f(d) = [(\gamma_0 - 1)^2 - 2d\,\gamma_0[d - (\gamma_0 - 1)^{-1}]] \tag{13}$$

Results:

Two binary mixtures 3Methylpentane+Nitreothane and Nitrobenzen-n Hexane use to studyFixman and Modification of Fixman analytic function at different frequency.

3Methylpentane+Nitreothane

Data of α_λ was taken from Garland and Sanchez paper (Garland and Sanchez, 1983), as well as the sound velocity.

Table (1): The necessary data which are needed to calculate $A_F(T)$ of 3methylpentane -nitrothane.

Quantity	Value	References
$\frac{}{T_C}$	299.6	(Abdelraziq, 2003)
$\overline{C_{pc}}$ (erg/gK)	1.94×10^{9}	(Greer and Hocken,1975)
c (rg/gK) $\xi_0(A)$	2.16	(Abdelraziq, 2003)
D_0 (cm^2/s)	3.28×10^{-8}	(Greer and Hocken, 1975)
ρ (g/cm^3)	0.791	(Abdelraziq, 2003)
ω^0 (Hz)	1.23×10^{11}	(Garland, 1983)
$\frac{}{}$	0.35	(Greer and Hocken, 1975)
$\frac{c}{}$	1.28	(Garland, 1983)

Figure(1) showplotsof experimentalabsorptionvalues $\frac{\alpha_\lambda}{u^2\ \pi A(T)}$ vs.reducedfrequencyω*ofFixman alongwiththe theoretical scaling integral $I(\omega*)$ of binary mixture 3Methylpentane+Nitreothane.
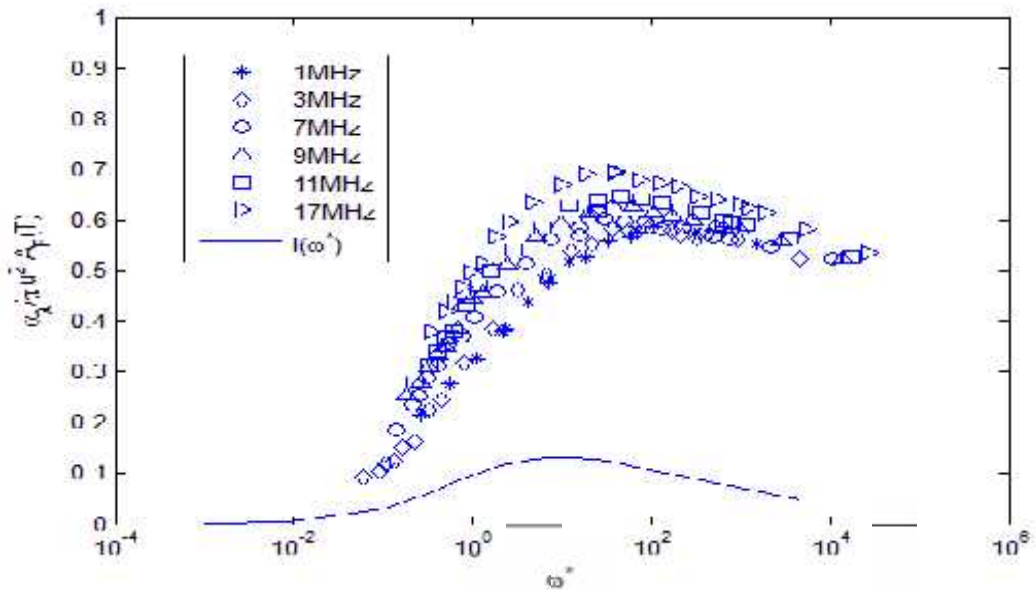
Fig.1.: Experimental absorption values $\frac{\alpha_\lambda}{\pi\,u^2 A_F(T)}$ Vs. reduced frequency ω^* for 3methylpentane+nitrothane according to Fixman theory along with the theoretical scaling integral $I(\omega^*)$.

Figure(2) showplotsof experimentalabsorptionvalues $\frac{\alpha_\lambda}{u^2\,\pi A(T)}$ vs.reducedfrequencyω*ofFixmanand Modification of Fixmanalongwiththe theoretical scaling integral $I(\omega^*)$ of binary mixture 3Methylpentane+Nitreothane.

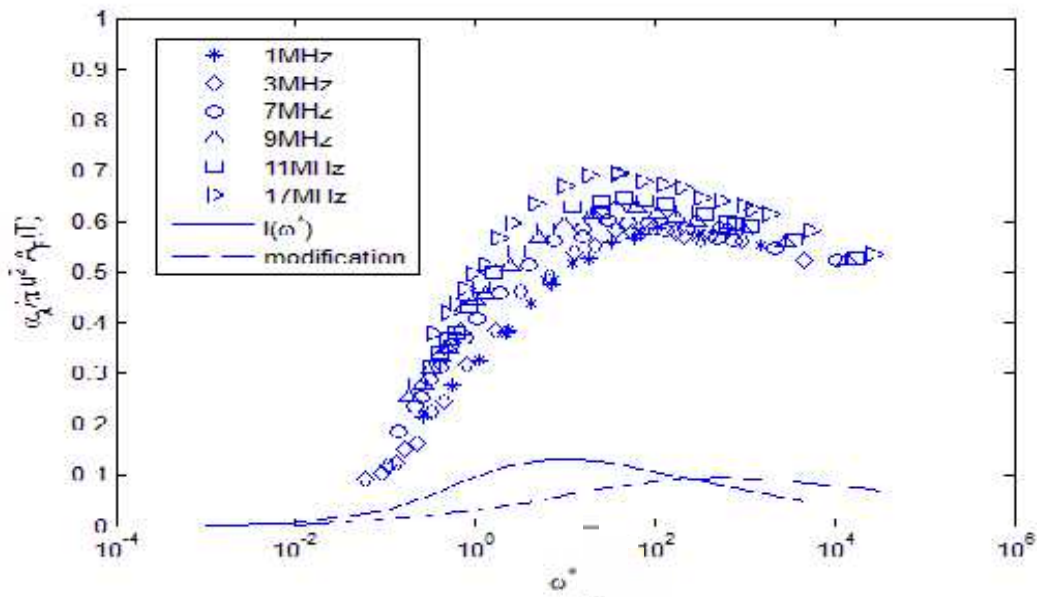**Fig.2.:.**Experimental absorption values $\frac{\alpha_\lambda}{\pi\,u^2 A_F(T)}$ Vs. reduced frequency for 3methylpentane+nitrothane according to Fixman theory along with the theoretical scaling integral $I(\quad)$ solid line, dashed line represent modification form of Fixman's theory.

Figure(3) showplotsof experimentalabsorptionvalues $\frac{\alpha_\lambda}{u^2\pi A(T)}$ vs. reducedfrequencyω*ofModification of Fixmanalongwiththe theoretical scaling integral I(ω*) of binary mixture 3Methylpentane+Nitreothane.
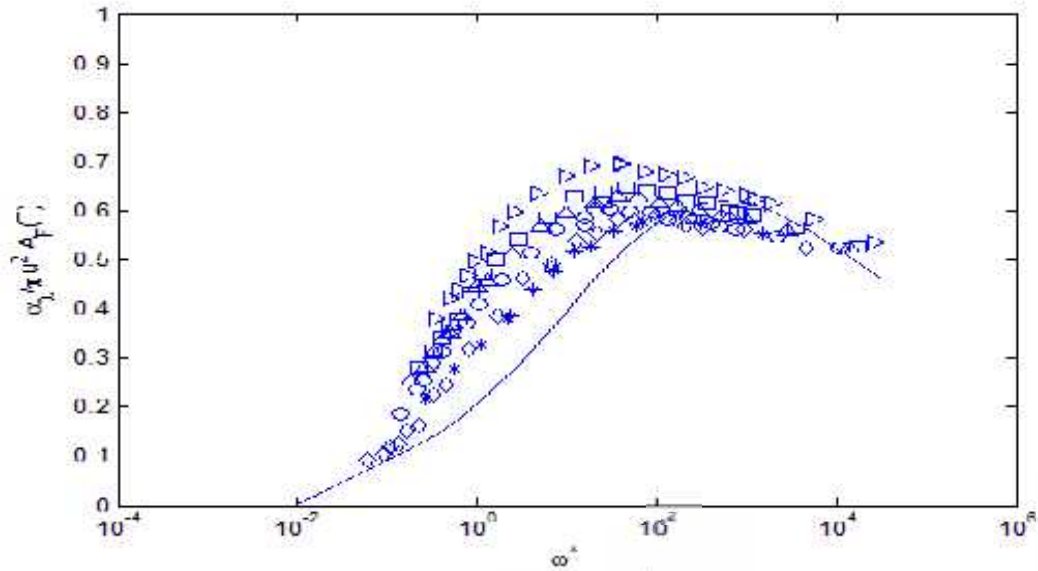

Fig.3.: Experimental absorption values $\frac{\alpha_\lambda}{\pi u^2 A_F(T)}$ Vs. reduced frequency ω^* for 3methylpentane+nitrothane according to modification Fixman theory along with the theoretical scaling integral I(ω^*) in solid line.

Nitrobenzen-n Hexane

Data of $\frac{\alpha_\lambda}{f^2}$ was taken from Abdelraziq (Abdelraziq, 1990), as well as the sound velocity.

Table (2): The necessary data which are needed to calculate $A_F(T)$ of Nitrobenzen- n Hexane

Quantity	Value	References
$\frac{T_{..}}{T c}$	293.25	(Abdelraziq, 2003)
C_{pc}(erg/gK)	$1.9^{3.25} \times 10^9$	(Greer and Hocken,1975)
$\frac{c^{..}(rg/gK)}{\xi^0(A)}$	2.03	(Abdelraziq, 2003)
$D_0 \left(\frac{cm^2}{s}\right)$	$3.28 \; 10_{-6}$	(Greer and Hocken, 1975)
ρ (g/cm^3)	0.8432	(Abdelraziq, 1989)
$\frac{g(..)}{\omega_0 \; Hz}$	$2^{1.84^2}_{..} \times 10^{10}$	(Abdelraziq, 1989)
$\frac{\omega^0(Hz)}{\eta^0 \; cp}$	0.563	(Abdelraziq, 1989)
$\frac{\mu}{c} \gamma^0$	1.24	(Abdelraziq, 1989)

Figure(4) show plotsof experimentalabsorptionvalues
$\frac{\alpha_\lambda}{u^2 \pi A(T)}$ vs.reducedfrequencyω*ofFixman alongwiththe theoretical scaling integral I
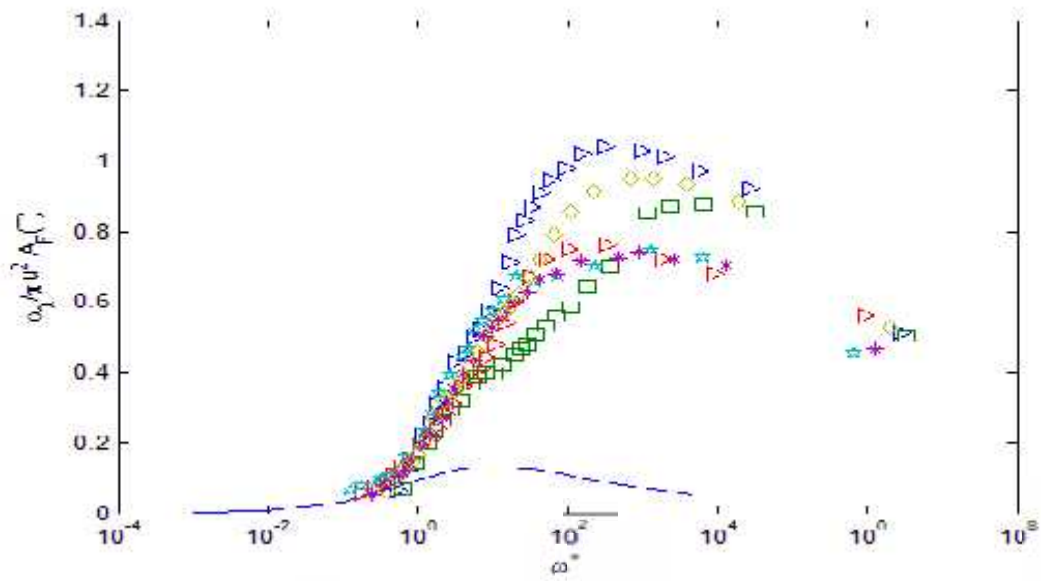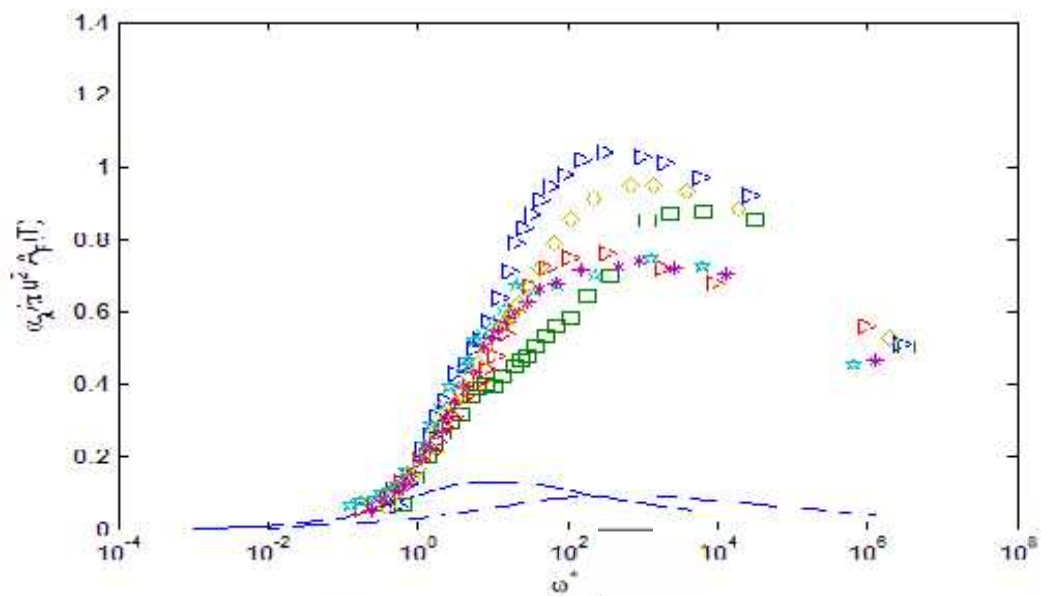(ω*) of binary mixture Nitrobenzen-n Hexane

Fig.4.: The experimental value $\frac{\alpha_\lambda}{\pi u^2 A_F(T)}$ Vs. reduced frequency ω^* for nitrobenzene- n hexane according to Fixman theory along with the theoretical scaling function $I(\omega^*)$ in solid line.

Fig.5 : The experimental value $\frac{\alpha_\lambda}{\pi u^2 A_F(T)}$ Vs. reduced frequency ω^* for nitrobenzene- n hexane according to Fixman theory along with the theoretical scaling function $I(\omega^*)$ [solid line], modification Fixman theory along with the theoretical scaling function $I(\omega^*)$ [dashed line].

Figure(6) show plotsof experimentalabsorptionvalues $\dfrac{\alpha_\lambda}{u^2\,\pi A(T)}$ vs.reducedfrequencyω*ofFixman alongwiththe theoretical scaling integral I $(\omega*)$ of binary mixture Nitrobenzen-n Hexane
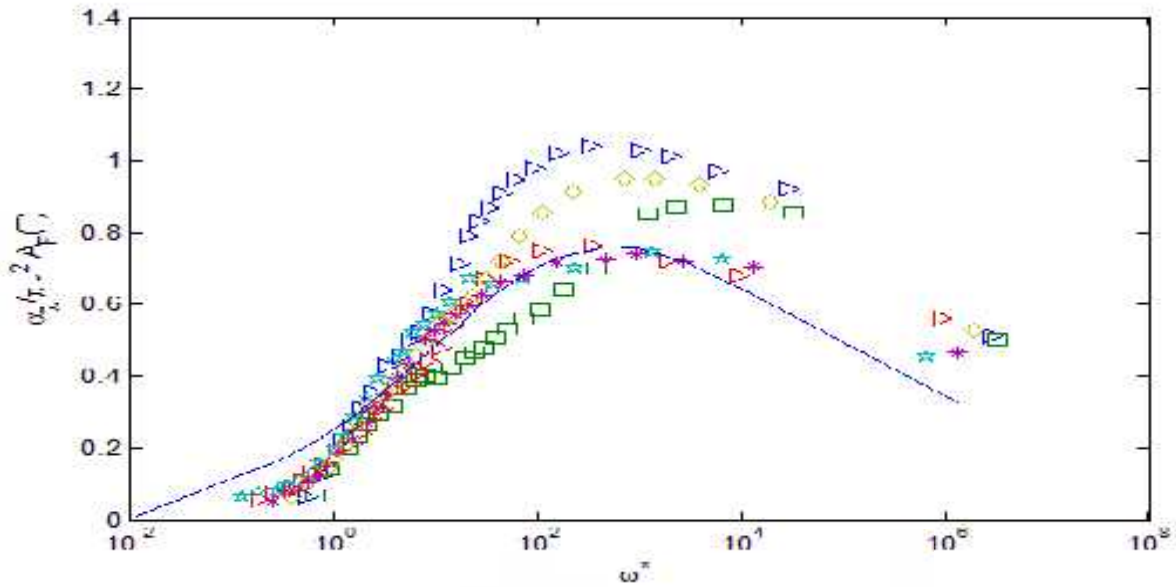

Fig.6.: The experimental value $\dfrac{\alpha_\lambda}{\pi u^2 A_F(T)}$ Vs. reduced frequency ω^* for nitrobenzene- n hexane according to modification Fixman theory along with the theoretical scaling function $I(\omega^*)$ in solid line with adding new parameter to scaling function.

Discussion:

Analytic function of Fixman theory is given by the following equation:

$$K(x) = x^2[1 + x^2]$$

Modification for Fixman analytic function is given by:

$$K(x) = 2x^2 * (10\,x^2 + 1 + 6x^4 + 8\,x^3) \qquad\qquad (14)$$

Where; γ_0: The ratio of heat capacities at constant pressure and volume, v: critical exponent equal 0.63. and $x = q\xi$, ξ:correlation length, q: wave number.

Closed to the critical point, the fluctuations in thermodynamic properties increase, then the system acting kindofarrangementafterthispoint, this behavior of binary system after this point is described by analytic function of mode coupling theories, which is proportional to the correlation length.

The analytic function of Fixman [equation (7)] is poor for describing this behavior of system below $\omega^* > 10$ or in high reduced frequency(closed to T_C), modification form of analytic function of Fixman's analytic function appear in equation (14), this

modification shows in figure (3) and figure (6), as noticed that new term in old analytic function caused a reductionin the amplitude of the scaling function, because this terms have relationship to the correlation length ξ which describe the range of fluctuations of thermodynamic properties of system after critical point, and this term cause Expansion in the scaling function as shown in figure 4.

The new term is not enough to match the theory to the experimental value, then need another term must be added to the scaling function after integration to raise the amplitude, this term depending on the ratio of heat capacities γ_0 which is equal $\frac{\gamma_0}{\gamma_0-1}+2.$

The results show a much better agreement in modification of Fixman analytic function thanthevaluesobtainedusingthetheoriesofFixman, especially at the low reduced frequencies ω^*.However,forthelargevaluesofreducedfrequency $\omega^*>10$the mode-couplingtheoryofFixmanstillexhibitspoor agreementwiththeobserveddata, but at modification of Fixman analytic function there is a good agreement at high frequency.

Conclusion

Mode-coupling theories used to describe the behavior of critical binary mixture after critical point, it have been disagreement with the experimental value of binary mixture over the range of reduced frequency $\omega^*>10$. The Modified-Fixman's theory was found much better than old Fixman's analytic function when applied it in binary mixtures 3Methylpentane+Nitreothane and Nitrobenzen-n Hexane.

The effective term which plays an important role in this modification depend on the ratio of heat capacities at constant volume and pressure $\gamma_0 = \frac{c_v}{c_p}.$

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