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Critical Amplitude of Acoustical Attenuation in Mode-Coupling Theory for the Binary Mixture Aniline and Cyclohexane

السعة الحرجة للإضمحلال الصوتي في نظرية الإزدواج للخليط الثنائي الانيلين - وسيكلوهكسين

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Abstract

Using Hornowski's theoretical modification of the critical amplitude, the experimental $\alpha_\lambda(crit)/\pi u(\omega)^2 A(T)$ values from mode-coupling theory of a binary liquid mixture aniline – cyclohexane have been compared with the theoretical expressions given by Fixman, Kawasaki, Mistura, and Chaban. The experimental data at low reduced frequencies ω^* has been found to agree well with the Hornowski's model of A(T). However, for the large values of reduced frequency $\omega^* > 10$ the mode-coupling theory of Shiwa and Kawasaki still exhibits poor agreement with the observed data, mainly due to the form of scaling function. The correlation length ξ_0 has been calculated by using ω_0 (the critical amplitude of the characteristic relaxation rate) which gives the best fitting to the theoretical critical amplitude. The adiabatic coupling constant g and the diffusion coefficient D_0 have been obtained using Hornowski's expression of the critical amplitude.

ملخص

لقد تم استخدام النتائج العملية المقاسة للسعة الحرجة للإضمحلال الصوتي في نظرية الإزدواج للخليط الثنائي للمقارنة بين نظرية هرنوسكي المعدلة والنظريات الأخرى وهي فيكسمان وكفازاكي ومستورا وشبان وقد أظهرت النتائج توافق جيد للسعة الحرجة لنموذج هرنوسكي عند الذبذبات الصغيرة. وكما أظهرت النتائج العملية ضعف في التوافق في نظرية الإزدواج لـِ شيفا وكفازاكي وسبب عدم التوافق هو الإقتران الاتزاني وكما تم حساب قيمة الطول الإرتباطي وثابت الإزدواج ومعامل الانتشار باستخدام نظرية هرنوسكي المعدلة للسعة الحرجة

Introduction

There are some theoretical models that predict the behavior of the sound propagation in the critical region of a binary liquid mixtures. They are known as renormalization group theory by Kroll and Ruhland [1], dynamic scaling theory by Bhattacharjee and Ferrell [2], mode-coupling theory by Fixman [3], Shiwa and Kawasaki [4], Mistura [5], and Chaban [6]. These mode-coupling theories failed to describe experimental data over a wide range of the reduced frequency ω^* [7]. This failure refers, firstly to inadequate in the scaling function of the acoustic attenuation $I(\omega^*)$ in its simple two-mode approximation at high reduced frequencies $\omega^* > 10$. Secondly the critical amplitude A(T) does not predict properly the strength of the critical attenuation by using the available thermodynamic data [8,9]. Hornowski *et al* [10] developed the modified version of the mode-coupling theory for the acoustic anomaly.

In this paper, the modified version by Hornowski *et al* [10] has been applied to describe the critical attenuation of the binary system of aniline and cyclohexane.

Theory

The mode-coupling theories lead to the same general expression for the attenuation per wavelength α_λ at critical concentration [4]

$$\alpha_\lambda/u^2(\omega)= \pi A(T)I(\omega^*) \quad (1)$$

Where $u(\omega)$ is the velocity of sound, A(T) is the critical amplitude and $I(\omega^*)$ 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 [4]:

$$I(\omega^*) = \int[y^2dy/\{1+y^2\}^2][\ \omega^* K(y)/\{K(y)^2+\omega^{*2}\}] \quad (2)$$

Where $\omega^* = \omega/\omega_D$ is the reduced frequency , ω_D is the characteristic frequency given by $\omega_D = 2D_0\xi_0^{-2}\ t^{1.93}$, K(y) is an explicitly known analytic function, D_0 is the diffusion coefficient and $t = (T-T_c)/T_c$ is the reduced temperature. In case of the the theories of Mistura, and Chaban K(y) is given by [9,11]

$$K(y) = ¾[1+y^2 +(y^3-1/y)\arctan(y)] \tag{3}$$

The Kawasak's analytic function is [9,12]

$K(y) = ¾[1+y^2 +(y^3-1/y)\arctan(y)][1.055^a + \{0.93 + 0.29 \log_{10}(y)\}^a]^{1/a}$ with the fitting exponent a = 13.

While the Fixman's analytic function is given by [3]

$$K(y) = y^2 [1+y^2] \tag{4}$$

The expression 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 [3,9,12]

$$A_F(T) = A_K(T) = [K_B(\gamma_0-1)\nu^2/ \pi\rho u\, C_{pb}\, \xi_0^3]t^{-\alpha} \tag{5}$$

Mistura's form of the critical amplitude is given by [9,11]

$$A_M(T) = A_F(T)[\gamma_0-1]^{-2}[1-0.5\eta]^2 \tag{6}$$

Chaban's form $A_C(T)$ is given by [6]

$$A_C(T) = A_F(T)\,[1-(\rho C_{pb}/\alpha_{pb})(dT_c/dP)]^2 \tag{7}$$

Where K_B is Boltzman's constant, ρ is the density of the mixture, C_{pb} is background heat capacity at constant pressure, $\gamma_0 = C_p/C_v$ is the ratio of heat capacities, α_{pb} is the background amplitude of the thermal expansion, ξ_0 is the correlation length, 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,ν,α are critical exponents.

Hornowski’s modification [10], similar to those of Fixman’s and Mistura’s has been based on the critical behavior of a relaxing complex heat capacity but more reliable assumptions concerning the contributions of the heat capacities at constant pressure C_P and constant volume C_v to the total relaxing heat capacity have been made. The general expression for the critical amplitude $A_H(T)$ has been derived in terms of the dimensionless parameter

$$d = [C_{vb}\rho/T\alpha_{pb}][dT_c/dP] \qquad (8)$$

where C_{vb} and α_{pb} are the background heat capacity and background thermal expansion coefficients.

The critical Hornowski’s amplitude $A_H(T)$ is given by [10]:

$$A_H(T) = A_K(T)\ [1 - 0.5\eta]^2\ f(d) \qquad (9)$$

Where the function $f(d) = |\ (\gamma_0 d-1)^2 - 2d\ \gamma_0\ [d-(\ \gamma_0-1)^{-1}]\ |$

and C_{vb} is the background term of specific heat at constant volume.

The adiabatic coupling constant g which was introduced by Ferrell and Bhattacharjee [2] can be defined interms of f(d) as shown in [13].

$$g^2 = \alpha_{pb}{}^2\, T^2\, |f(d)| \qquad (10)$$

Results and Discussion

Measurements of absorption were made using the matec pulse-echo technique that generates pulses through the temperature-controlled test cell. Setup and operational procedure are discussed in our previous papers [14-19]. The binary mixture aniline and cyclohexane has an upper critical temperature of $T_c = 30.20\,^{\circ}C$ and a critical composition of 47.0 wt % aniline [8,18]. The ultrasonic absorption was measured for frequencies 5, 7, 10, and 15 MHz. The temperature of the sample was controlled within $\pm$ 0.01 $^{\circ}C$.

The necessary collateral data in table (1) enable us to calculate A(T) of each theory.

Table 1: The necessary collateral data which are needed to calculate A(T) of each theory.

Quantity	Value	Reference
T_c (K)	303.36	8
C_{pb} (erg/gK)	2.04 X 10^7	18
C_{pc} (erg/gK)	0.27 X10^7	18
G	-0.13	18
α_{pc} (K^{-1})	0.49 X10^{-4}	18
ξ_0 ( )	2.2	21
dT_c/dP (K cm^2/dyne)	0.68 X 10^{-8}	8
ρ (g/cm^3)	0.860	8
γ_0	1.31	8
ω_0(Hz)	3.28 X10^{10}	18
u (cm/s)	132621	18
ν	0.62	19, 22, 23
η	0.04	19, 22, 23
α	0.11	19, 22, 23

Figures (1-5) show plots of experimental absorption values $\alpha_\lambda/\pi u^2(\omega)A(T)$ vs. reduced frequency ω^* of Fixman, Kawasaki, Mistura, Chaban and Hornowski *et al* expressions, respectively, along with the theoretical scaling integral $I(\omega^*)$.

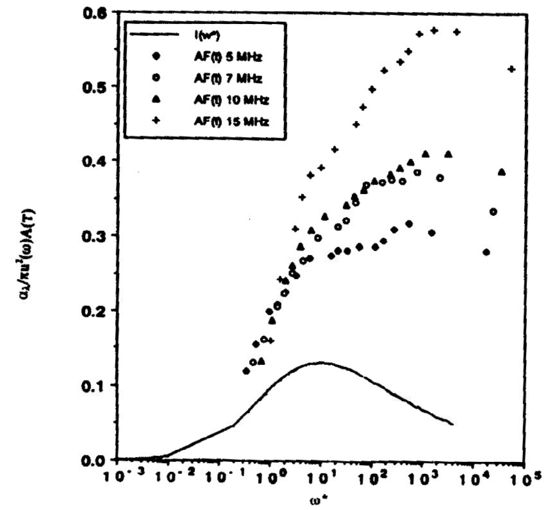

Figure 1: The experimental absorption values $\alpha_\lambda/\pi u^2(\omega)A(T)$ Vs. reduced frequency ω* for aniline – cyclohexane mixture according to Fixman theory along with the theoretical scaling integral I(ω*).

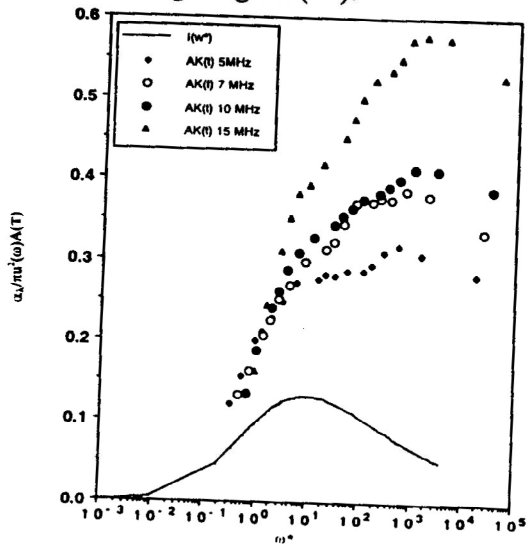

Figure 2: The experimental absorption values $\alpha_\lambda/\pi u^2(\omega)A(T)$ Vs. reduced frequency ω* for aniline – cyclohexane mixture according to Kawasaki theory along with the theoretical scaling integral I(ω*).

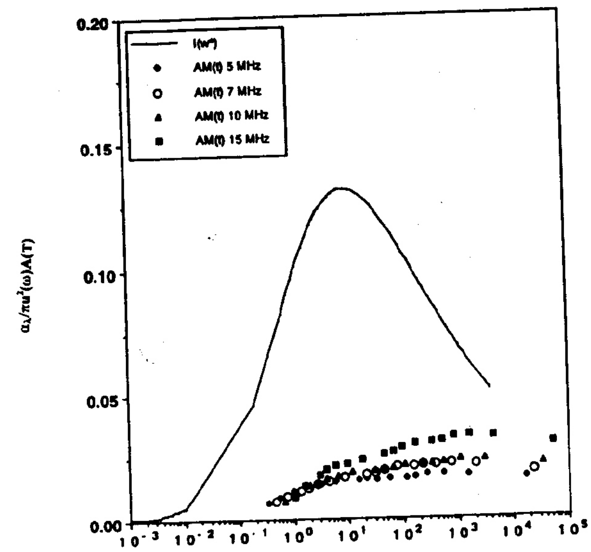

Figure 3: The experimental absorption values $\alpha\lambda/\pi u^2(\omega)A(T)$ Vs. reduced frequency ω^* for aniline – cyclohexane mixture according to Mistura theory along with the theoretical scaling integral $I(\omega^*)$.

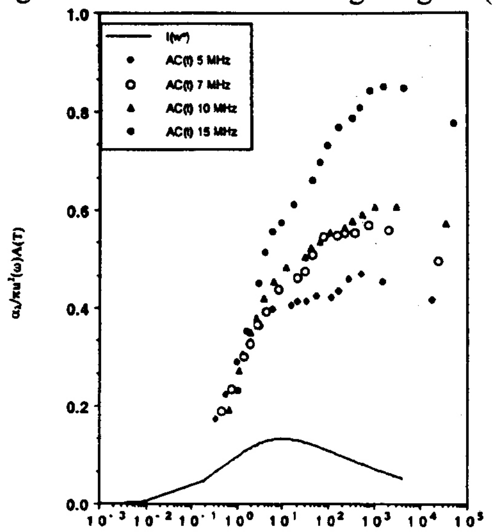

Figure 4: The experimental absorption values $\alpha\lambda/\pi u^2(\omega)A(T)$ Vs. reduced frequency ω^* for aniline – cyclohexane mixture according to Chaban theory along with the theoretical scaling integral $I(\omega^*)$.

0.3

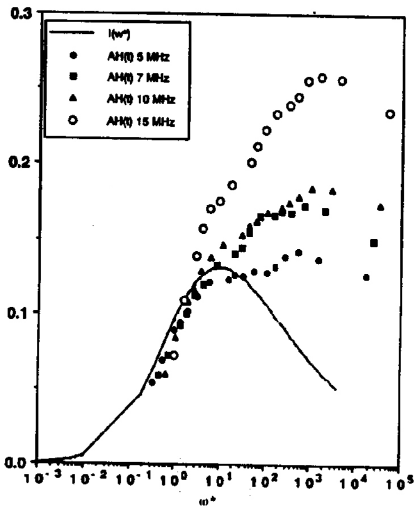

Figure 5: The experimental absorption values $\alpha_\lambda/\pi u^2(\omega)A(T)$ Vs. reduced frequency ω^* for aniline – cyclohexane mixture according to Hornowski *et al* theory along with the theoretical scaling integral $I(\omega^*)$.

Γ) Vs. ding to ω*).

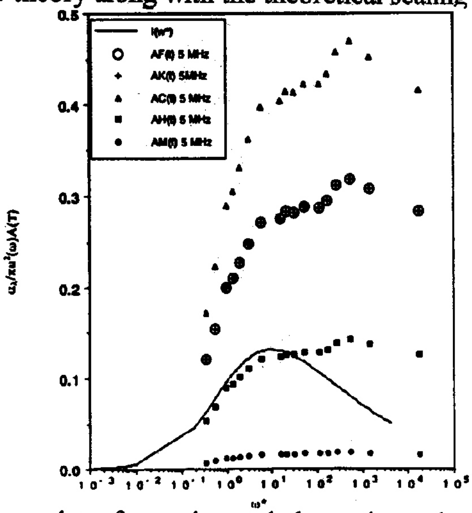

Figure 6: shows a plot of experimental absorption values $\alpha_\lambda/\pi u^2(\omega)A(T)$ Vs. ω^* at 5 MHz for all the expressions together along with the theoretical scaling integral $I(\omega^*)$.

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The results show a much better agreement in Hornowski *et al* modification than the values obtained using the theories of Fixman, Kawasaki, Mistura, and Chaban especially at the low reduced frequencies ω^*. However, for the large values of reduced frequency $\omega^* > 10$ the mode-coupling theory of Shiwa and Kawasaki still exhibits poor agreement with the observed data, mainly due to the form of scaling function characteristics.

The adiabatic coupling constant g = -0.15 has been calculated and compared to the g = -0.13 obtained by Abdelraziq [18] using the dynamic scaling theory. They are in good agreement. The adiabatic coupling constant g is a negative value which implies that phase separation can be induced by a sudden decrease in pressure.

The correlation length ξ_0 and the diffusion coefficient D_0 have been obtained by using Hornowaski's expression of the critical amplitude. The correlation length is in good agreement compared to values obtained by Perge *et al*[20] and Lai *et al*[21]. Tables (1) and (2) show the calculated values in this work and other references.

Table 2: The calculated values in this work and other references.

Quantity	Calculated	Reference
d	0.378	
f(d)	3.075	
ξ_0 ( )	2.25 ± 0.1	2.11^a, 2.20^b
$D_0(cm^2/s)$	9.24×10^{-6}	
g	-0.15	-0.13^c

[a](Ref 20) [b](Ref 21) [c](Ref 18)

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