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

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Abstract

Using Hornowski’s theoretical modification of the critical amplitude, the experimental \( \alpha_c(\text{crit})/\pi u(\omega)_2 A(T) \) 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 \( \omega^* \) 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 \( \xi_0 \) has been calculated by using \( \omega_0 \) (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.

Malłąş

لقد تم استخدام النتائج العملية المقدمة للسرعة الحرجة للإضمحلال الصوتي في نظرية الإدزاج للكليط الثاني لمقارنة بين نظرية هرونوسكي المعهولة والنظريات الأخرى وهي فيكسمان وكازافاك ومستورا وشنان وقد أظهرت النتائج توافق جيد للسرعة الحرجة لنموذج هرونوسكي عند النصبات الصغيرة. وكما أظهرت النتائج العملية ضعف في التوافق في نظرية الإدزاج لـ شيفا وكازافاك وسبب عدم التوافق هو الإقتران الإرادي كما تم حساب قيمة الطول الإرادي وثابت الإدزاج ومعامل الانتشار باستخدام نظرية هرونوسكي المعهولة للسرعة 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 $\omega^*$ [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 $\alpha_\lambda$ at critical concentration [4]

$$\alpha_\lambda/\lambda^2(\omega) = \pi A(T) I(\omega^*)$$  \hspace{1cm} (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]:

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

Where $\omega^* = \omega/\omega_D$ is the reduced frequency, $\omega_D$ is the characteristic frequency given by $\omega_D = 2D_0\tilde{\omega}_0^{-2}t^{1.93}$, $K(y)$ 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]

$$K(y) = \frac{3}{4}[1+y^2 + (y^3-1/y)\arctan(y)] \tag{3}$$

The Kawasaki’s analytic function is [9,12]

$$K(y) = \frac{3}{4}[1+y^2 + (y^3-1/y)\arctan(y)][1.055^a + \{0.93 + 0.29 \log_{10}(y)\}^a]^{1/a}$$

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]

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

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, $\rho$ 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, $\alpha_{pb}$ is the background amplitude of the thermal expansion, $\xi_0$ 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 $\eta, \nu, \alpha$ 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

\[
d = \left[ \frac{C_{vb}}{\gamma_0 \rho \alpha_{pb}} \right] \frac{dT}{dP}
\]

(8)

where \( C_{vb} \) and \( \alpha_{pb} \) are the background heat capacity and background thermal expansion coefficients.

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

\[
A_H(T) = A_K(T) \left[ 1 - 0.5 \eta \right]^2 f(d)
\]

(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 in terms of \( f(d) \) as shown in [13].

\[
g^2 = \alpha_{pb}^2 T^2 |f(d)|
\]

(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.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_c ) (K)</td>
<td>303.36</td>
<td>8</td>
</tr>
<tr>
<td>( C_{pb} ) (erg/gK)</td>
<td>2.04 \times 10^7</td>
<td>18</td>
</tr>
<tr>
<td>( C_{pe} ) (erg/gK)</td>
<td>0.27 \times 10^7</td>
<td>18</td>
</tr>
<tr>
<td>( G )</td>
<td>-0.13</td>
<td>18</td>
</tr>
<tr>
<td>( \alpha_{pe} ) (K(^{-1}))</td>
<td>0.49 \times 10^{-4}</td>
<td>18</td>
</tr>
<tr>
<td>( \xi_0 ) (Å)</td>
<td>2.2</td>
<td>21</td>
</tr>
<tr>
<td>( \frac{dT_c}{dP} ) (K cm(^2)/dyne)</td>
<td>0.68 \times 10^{-8}</td>
<td>8</td>
</tr>
<tr>
<td>( \rho ) (g/cm(^3))</td>
<td>0.860</td>
<td>8</td>
</tr>
<tr>
<td>( \gamma_0 )</td>
<td>1.31</td>
<td>8</td>
</tr>
<tr>
<td>( \omega_0 ) (Hz)</td>
<td>3.28 \times 10^{10}</td>
<td>18</td>
</tr>
<tr>
<td>( u ) (cm/s)</td>
<td>132621</td>
<td>18</td>
</tr>
<tr>
<td>( \nu )</td>
<td>0.62</td>
<td>19, 22, 23</td>
</tr>
<tr>
<td>( \eta )</td>
<td>0.04</td>
<td>19, 22, 23</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.11</td>
<td>19, 22, 23</td>
</tr>
</tbody>
</table>

Figures (1-5) show plots of experimental absorption values \( \alpha_{\lambda}/ru^2(\omega)A(T) \) vs. reduced frequency \( \omega^* \) 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 $\frac{\alpha_0}{\pi u^2(\omega)} \Delta(T)$ Vs. reduced frequency $\omega^*$ for aniline – cyclohexane mixture according to Fixman theory along with the theoretical scaling integral $I(\omega^*)$.

Figure 2: The experimental absorption values $\frac{\alpha_0}{\pi u^2(\omega)} \Delta(T)$ Vs. reduced frequency $\omega^*$ for aniline – cyclohexane mixture according to Kawasaki theory along with the theoretical scaling integral $I(\omega^*)$. 

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

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

Figure 5: The experimental absorption values $\frac{\alpha}{\mu s^2(\omega)}A(T)$ Vs. reduced frequency $\omega^*$ for aniline – cyclohexane mixture according to Hornowski et al. theory along with the theoretical scaling integral $I(\omega^*)$.

Figure 6: Shows a plot of experimental absorption values $\frac{\alpha}{\mu s^2(\omega)}A(T)$ Vs. $\omega^*$ at 5 MHz for all the expressions together along with the theoretical scaling integral $I(\omega^*)$.
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 \( \omega^* \). 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 \( \xi_0 \) 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.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Calculated</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d )</td>
<td>0.378</td>
<td></td>
</tr>
<tr>
<td>( f(d) )</td>
<td>3.075</td>
<td></td>
</tr>
<tr>
<td>( \xi_0 ) (Å)</td>
<td>2.25 ± 0.1</td>
<td>2.11(^a), 2.20(^b)</td>
</tr>
<tr>
<td>( D_0 ) (cm(^2)/s)</td>
<td>9.24 X10(^{-6})</td>
<td></td>
</tr>
<tr>
<td>( g )</td>
<td>-0.15</td>
<td>-0.13(^c)</td>
</tr>
</tbody>
</table>

\(^{a}(\text{Ref 20})\) \(^{b}(\text{Ref 21})\) \(^{c}(\text{Ref 18})\)

### References