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

Saja Omar and IssamAbdelraziq*

Physics Dept. AnNajah National University, Nablus, Palestine

Corresponding Author: IssamAbdelraziq

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 $T_c = 45.2$ °C 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 $\alpha_c$ at different frequencies. The linear relation of $\frac{\alpha_c}{\gamma^2}$ versus $-1.06$ was obtained. The adiabatic coupling constant g, isobaric thermal expansion coefficient $\alpha_p$ 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 $\omega^*$ and it showed a good agreement with the theoretical scaling function $F(\omega^*)$ presented by Ferrell and Bhattacharjee.
**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 ¹.

**Liquid Systems**

There are two types of liquid systems; first is the pure one which is 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, ². 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 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.

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.  

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 ≤ T-T_c ≤ 13.5K. 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.  

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 (\( \frac{g}{r^2} \)) versus \( r^{-1.06} \) was proved to be straight line according to the dynamic scaling theory. The adiabatic coupling constant (\( g \)) has been evaluated by Fast and Yun.  

Jacobs has measured the turbidity of the critical mixture methanol – cyclohexane above its critical point. The correlation length \( \xi \) was calculated using the two scale factor universality.  

Ferrell found that the sound propagation produce temperature swings if the frequency is smaller than the relaxation time.  

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 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.

The ultrasonic absorption coefficient $\alpha$ 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 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 studied the ultrasonic absorption at 5 - 25MHz frequency range and velocity measurements above the critical temperature for perfluoromethylcyclohexane - carbon tetrachloride.

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

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.

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.
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 \(^{17}\).

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 \(^{18}\).

**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.

**Theory**

This paper is based on the dynamic scaling theory which proposed by Ferrell and Bhattacharjee to study the ultrasonic attenuation in binary liquid mixtures\(^4\).

In the dynamic scaling theory the total absorption coefficient at the critical temperature and concentration can be simply expressed as \(^{3, 4, 13, 18}\)

\[
\frac{\alpha(x_c, T_c)}{\epsilon^2} = S \cdot 1.06 + b
\]

where \(b\) represents the contribution of the frequency independent background absorption. The \(S\) value is given by \(^{3, 4, 13, 18}\).
Here $\gamma = 0.11$ and $\gamma = 1.9$ are the critical exponents, $C_{pc}$ is the critical amplitude in the following expression for the specific heat at constant pressure of a mixture of critical composition $^{3,13,18}$

$$C_p = C_{pc} t^{-\gamma} + C_{pb}$$

$C_{pb}$ is the background specific heat, $a$ is a dimensionless scaling factor of order unity, $\omega_0$ is a characteristic temperature-dependent relaxation rate, $g$ is the adiabatic coupling constant, $u_c$ is the adiabatic sound velocity at $T_c$, and $C_p(t_f)$ is the specific heat at a characteristic reduced temperature $t_f$, which can be approximated by $t = \frac{T-T_c}{T_c}$.

The adiabatic coupling constant $g$ was introduced by Ferrell and Bhattacharjee and is given by $^{3,4,13,18}$:

$$g = \rho_c C_p \left( \frac{4T_c}{dP} - \frac{T\alpha_p}{\rho C_p} \right)$$

where $\rho_c$ is the density at critical temperature and concentration and $\alpha_p$ is the isobaric thermal expansion coefficient.

The absorption coefficient $\alpha(crit,\omega,T)$ can also be expressed as a function of the dimensionless reduced frequency $\omega^* = \frac{\omega}{\omega_D}$, $^{3,4,13,18}$

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

where $\omega_D$ is given by:

$$\omega_D = \frac{K_3 T_c}{3\pi \eta^3} = \frac{K_3 T_c}{3\pi \eta^3 \xi_0} (z\gamma - \omega_0 t^{2\gamma})$$

Here $k_B$ is Boltzmann’s constant, $\xi$ is the correlation length and $\eta$ is the shear viscosity.
**Data Analysis:**

The viscosity of binary liquid mixture methanol –cyclohexane is measured as a function of temperature using Brookfield viscometer. The critical temperature and critical concentration is determined.

The data of ultrasonic absorption coefficient were fitted using excel program by plotting $\alpha_c/\gamma^2$ versus $-1.06$. Absorption coefficients at the critical concentration and any temperature data were taken at different frequencies [5 and 25MHz]. The relation of $\alpha_c/\gamma^2$ versus T (°C) was plotted. The scaling function is plotted as a function of reduced frequency for the methanol – cyclohexane system.

**Results and Analysis**

The critical concentration and critical temperature is obtained for the binary liquid mixture methanol – cyclohexane to be 30% by weight of methanol as critical concentration and 45.2°C as critical temperature. Shear viscosity is obtained to be 0.83cP as shown in Fig. (1)
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:

$$ R = \xi_0 \left( \frac{\rho_c C_P}{k_B} \right)^{1/3} = 0.27 $$

(1)

Where: $\bar{\eta} = 0.11$, $K_B = 1.3806 \times 10^{-23} \text{ J K}^{-1}$ and $\xi_0 = 3.24 \times 10^{-10} \text{ m}^7$

Calculation of the Adiabatic Coupling Constant $g$

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

$$ g = \rho_c C_P \left( \frac{dT_c}{dT} - \frac{T_c}{\rho C_P} \right) $$

(2)
Using $\rho_c = 0.7695 \, \text{g/cm}^3$, $\gamma_c = 9.4239 \times 10^5 \, \text{erg/}^0\text{C} \cdot \text{g}$, $\frac{dT_c}{dP} = 3.4 \times 10^{-8} \, \text{cm}^2 \, \text{g}^{-1} \, \text{dyne}$, $T = 45.2^\circ\text{C}$ and $\alpha_p = \rho \times 9.1 \times 10^{-3} \, ^0\text{C}^{-1}$

g = - 0.29

**Ultrasonic Attenuation Results**

The binary liquid mixture methanol – cyclohexane has a critical temperature at $45.2^\circ\text{C}$. The absorption measurements were made for the frequencies 5 and 25MHz in the critical concentration sample of 30% by weight of methanol above the critical temperature.

![Graph showing absorption coefficient $\alpha f / f^2$ vs temperature T.](image)

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

Ferrell and Bhattacharjee in the theory of the dynamic scaling proposed that the relation between $\frac{\alpha f}{f^2}$ and $T^{-1.06}$ is fitted linearly for different values of frequency at the critical concentration and temperature. Values of the critical absorption coefficient $\alpha_c$ at different frequencies from 5 – 45MHz.
Fig. (3): The absorption coefficient $\frac{\alpha}{f^2}$ or critical mixture methanol – cyclohexane as function of $f^{-1.06}$.

The slope from Fig. (3) represents the critical part of the attenuation is to be $1.8452 \times 10^{-7} \text{cm}^{-1} \text{s}^{0.94}$ and the value of the intercept which represents the frequency – independent background term of $\frac{\alpha}{f^2}$ is $5.5668 \times 10^{-15} \text{cm}^{-1} \text{s}^2$.

The magnitude of the slope from Fig. (3) is expressed as:

$$\text{Slope (S)} = \left[ \frac{\pi^2 c \sigma \varepsilon^2}{2 \gamma \gamma_c \varepsilon_0} \right] \left[ \frac{2 \omega_0}{2 \pi} \right] = 1.8452 \times 10^{-7} \text{cm}^{-1} \text{s}^{0.94}. \quad (3)$$

The characteristic temperature – dependent relaxation rate $\omega_0$ is $3.5959 \times 10^{10} \text{s}^{-1}$.

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

$$a = \left( \frac{\omega}{\omega_0} \right) t_f^{-1.9} \quad (4)$$

The values of the dimensionless constant $a$ from Fig. (2) at the frequencies 5 and 25MHz are:
\[ a(5\text{MHz}) = \frac{5 \times 10^6}{3.5959 \times 10^{10}} (0.1283)^{1.9} = 6.8772 \times 10^{-3} \text{ and} \]
\[ a(25\text{MHz}) = \frac{25 \times 10^6}{3.5959 \times 10^{10}} (0.1504)^{1.9} = 5.0834 \times 10^{-3}. \]

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 25 MHz using equation (3) as:

\[ C_p(t_f)(5\text{MHz}) = 2817.07 \frac{J}{Kg \text{de}l} \]
\[ C_p(t_f)(25\text{MHz}) = 1698.01 \frac{J}{Kg \text{de}l} \]

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

\[ F(\omega^*) = (1 + \omega^{*0.5})^{-2} \quad (5) \]

The experimental data \(^20\) 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.
**Diffusion Coefficient Calculation:**

The diffusion coefficient $D_0$ is calculated using the relation below:

$$\omega_0 = 2D_0 \tilde{\omega}_0^{-2}$$

(6)

This equation was suggested by Kawasaki$^{21}$ and Ferrell$^8$

At the critical temperature $D_0$ is calculated to be $1.89 \times 10^{-5}$ cm$^2$/s

**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$^\circ$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 $T_c = 45.1 \degree C$. 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 $T_c = 45.7 \degree C$. 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$\degree C$ respectively.

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 $C_{pc} = 94.24 \dfrac{J}{K \cdot Kg}$ and it showed a good agreement with Kopelman teams' value of $C_{pc} = 95.4 \dfrac{J}{K \cdot Kg}$. 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 $769.5 \dfrac{kg}{m^3}$.

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 $|0.21|$. 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 $\alpha_p$ is $7.00 \times 10^{-3} \, \degree C^{-1}$ while Behrends value was $1.28 \times 10^{-3} \, \degree C^{-1}$. The difference between our value of the isobaric thermal expansion coefficient $\alpha_p$ 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. 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 ($\alpha_c, \alpha_b$) and because of the difference in the magnitude of
\[
\frac{d\alpha_c}{dP} \quad \text{and} \quad \alpha_b.
\]

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$^{13}$.

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°C for
5MHz and 52°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 $6.8772 \times 10^{-3}$ at 5MHz and $5.0834 \times 10^{-3}$ 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 $\Delta T^4$.

The results of ultrasonic attenuation showed a linear behavior when $\frac{\alpha}{\alpha_c}$ is plotted versus $f^{-1.06}$. The linear relation of the plotted data is in good agreement with the dynamic scaling theory which predicts this behavior. The slope of the plotted data of $\frac{\alpha}{\alpha_c}$ versus $f^{-1.06}$ is $1.8452 \times 10^{-7}$ cm$^{-1}$ s$^{0.94}$ and the intercept is $5.5668 \times 10^{-15}$ cm$^{-1}$ 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 $F(\omega^*) = (1 + \omega^{*-0.5})^{-24}$. It is found that the experimental results of $\frac{\alpha}{\alpha_c}$ are in good agreement with the theoretical assumption by Ferrell and Bhattacharjee. 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 $\omega_0$ was calculated and it is found to be $3.5959 \times 10^{10}$ s$^{-1}$. The value of $\omega_0$ according to the dynamic scaling theory is calculated when the energy decay rate of a fluctuation is at $\xi^{-1.4}$.

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 (1).
Table (1): Ultrasonic attenuation results in this work and previous studies.

<table>
<thead>
<tr>
<th>The measured and calculated value</th>
<th>Our results</th>
<th>Other work</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_c^*$</td>
<td>30%</td>
<td>29.0% $^{(a)}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27.5% $^{(b)}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28.9% $^{(c)}$</td>
</tr>
<tr>
<td>$T_c^*$</td>
<td>45.2°C</td>
<td>45.1°C $^{(a)}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45.7°C $^{(b)}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45.9°C $^{(c)}$</td>
</tr>
<tr>
<td>$C_{pc}^*$</td>
<td>94.24 $^{-1}$</td>
<td>95.4 $^{-1}$ $^{(d)}$</td>
</tr>
<tr>
<td>$g^{**}$</td>
<td>-0.29 (1st method)</td>
<td>0.21 $^{(b)}$</td>
</tr>
<tr>
<td>$\alpha_p^{**}$</td>
<td>$7.00 \times 10^{-4}$</td>
<td>$1.28 \times 10^{-4}$ $^{(a)}$</td>
</tr>
<tr>
<td>$\alpha_{pc}^{**}$</td>
<td>$3.797 \times 10^{-4}$</td>
<td>–</td>
</tr>
<tr>
<td>$\rho_c^*$</td>
<td>0.7695 g/ml</td>
<td>–</td>
</tr>
<tr>
<td>$\eta_o^*$</td>
<td>0.83 cP</td>
<td>–</td>
</tr>
<tr>
<td>$D_o^{**}$</td>
<td>$1.89 \times 10^{-5}$ cm$^2$/s</td>
<td>–</td>
</tr>
<tr>
<td>$u_c^*$</td>
<td>$1062 \frac{m}{s}$</td>
<td>–</td>
</tr>
</tbody>
</table>

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


3Iwanowski I., “Critical behavior and crossover effects in the properties of binary and ternary mixtures and verification of the dynamic scaling conception”, dissertation, GeorgiaAugusta University, (2007)


