

Debye momentum cutoff of the critical binary mixture of carbon tetrachloride and coconut oil

Yusur.H.Kittany*, Issam.R.Abdelraziq

Department of Physics, AN-Najah National University, Nablus, (STATE OF PALESTINE)

ABSTRACT

The dynamic shear viscosity coefficients of the binary liquid mixture carbon tetrachloride and coconut oil for different temperatures and concentrations are measured using digital viscometer with UL adapter. Shear viscosity anomaly is clearly observed near the critical temperature $T_c = 22.2^\circ\text{C}$ and the critical concentration $x_c = 0.732$ by weight of carbon tetrachloride. Debye parameter L (the intermolecular force range) was calculated using a light scattering formula to be $L = 5.5 \text{ \AA}$. Mode Coupling Theory (MCT) of the dynamic shear viscosity is used to fit our experimental data above the critical temperature in the range $0.05 \leq T - T_c \leq 8^\circ\text{C}$. It is found that the noncritical part of the dynamic shear viscosity (background viscosity) $\eta_0 = 2.59 \text{ cP}$ and the Debye momentum cutoff (the upper cutoff wave number) $q_D = 0.126 \text{ \AA}^{-1}$. The MCT universal constant A is measured to be $A = 0.054$ which is consistent with the theoretical value. © 2015 Trade Science Inc. - INDIA

INTRODUCTION

Viscosity

Viscosity is one of the main subjects of Rheology; the science that interested in the study of deformation and flow of matter. It is a measure of a fluid (gas or liquid) internal resistance to flow and it refers to the internal friction force between adjacent layers of a fluid, such friction opposes the development of velocity differences within the fluid layers. Viscosity is affected by the temperature and the composition of the fluid and, for compressible fluid, also by pressure.

The viscosity of liquid in general decreases with increasing temperature; the relationship can be expressed in the form of Duhne logarithmic equation [15].

$$\log \eta = C + \frac{B}{T} \quad (1)$$

Where η is the dynamic shear viscosity in cP, T : is the absolute temperature in K, and the constants (C and B) are characteristics of each material.

The kinematic shear viscosity ν is defined as the dynamic shear viscosity divided by the density of the liquid ρ at the same temperature and pressure [26]:

$$\nu = \frac{\eta}{\rho} \quad (2)$$

with the unit of (Stokes = $10^{-4} \text{ m}^2/\text{sec}$), usually measured in Centistokes (cSt).

Binary mixtures

A binary liquid mixture is a combination of two pure liquid substances, which have a limited solubility of each one in the other [24], like CCl_4 -coconut oil. The temperature and concentration above which the two liquids become completely miscible at all proportions called critical temperature T_c and critical concentration x_c . This point; where phase transi-

Full Paper

tion occurs, is called the critical point.

Experiments show that certain thermodynamic and transport properties of a binary liquid mixture like shear viscosity, heat capacity and thermal expansion coefficient behave anomalously in the vicinity of the critical point.

I Light scattering results

Light scattering experiment was used by Debye to study the critical binary mixtures. The correlation length ξ , the intermolecular force range L (Debye parameter) and the cutoff coupling wave vector q_D (Debye momentum cutoff) between the mixture molecules was defined extensively. He predicted the divergence of the correlation length (which measures the range of concentration fluctuations in real space) as T approaches T_c [15, 13]:

$$\xi = \xi_0 \tau^{-\nu} \quad (3)$$

where ξ_0 is the critical amplitude of the correlation length of the concentration fluctuations and it is a

characteristic of each binary mixture, $\tau (= \frac{T - T_c}{T_c})$ is the reduced absolute temperature which measures the distance from the critical temperature T_c and $\nu (= 0.64)$ is a critical exponent [14, 21, 4, 6, 2, 5, 3]. This can be described as follows; in approaching the critical temperature, not only the amplitude of the fluctuations, but also their correlation length increases.

Light scattering experiments also predict that around the critical point, a relation between the correlation length ξ and the intermolecular force range L of the following form should be exist [15]:

$$\xi^2 = \frac{L^2}{\tau} \quad (4)$$

Klein and Woermann show that the modified form of Eq.(4) is [21]:

$$L = 2.45 \xi_0 T_c \frac{(\nu-1)}{2} \quad (5)$$

Where $\nu (= 1.25)$ is the universal critical exponent of the isothermal compressibility and T_c is the critical temperature for the binary system in K.

II Dynamic Shear Viscosity MCT

MCT predicts a divergence of the kinetic coefficients near the critical point, one of the kinetic transport coefficients is the dynamic shear viscosity

η . To describe the divergence of η near the critical point, two contributions must be considered: the critical part; which is dominant near the critical point, and the regular part; which is dominant far away from it. Then, the dynamic shear viscosity η near the critical point can be written as a power law [19, 20]:

$$\eta = \eta_0 \tau^{-\nu_{\eta}} \quad (6)$$

Where, τ is the reduced absolute temperature, η_0 is the noncritical part of the dynamic shear viscosity in cP, and ν_{η} is the critical exponent for the viscosity anomaly and it is equal to 0.04 [21, 1, 10, 9, 7, 8].

The MCT of Perl and Ferrell predicts the logarithmic temperature dependence of the hydrodynamic shear viscosity near the critical point (Perl and Ferrell; 1972):

$$\frac{\Delta\eta}{\eta} = \frac{(\eta - \eta_0)}{\eta} = A \ln(q_D \xi) \quad (7)$$

Where $\frac{\Delta\eta}{\eta}$ is the relative anomalous dynamic shear viscosity, η is the dynamic shear viscosity at the critical concentration in cP, η_0 is the background viscosity, A is a MCT universal constant predicted to have

the theoretical value $0.054 = \frac{8}{15\pi^2 [176]}$, q_D is the upper cutoff wave number (Debye momentum cutoff) in \AA^{-1} and ξ is the correlation length of the concentration fluctuations in \AA .

EXPERIMENTAL

Methodology

The two high purified chemicals of CCl_4 and coconut oil are used to prepare the samples of the binary mixture with different concentrations. The viscosity of the samples is measured over the entire concentration range and for a wide range of temperatures using digital viscometer with UL adapter. The experimental results are fitted statistically using Excel program. The critical point is determined. Data near the critical point is analyzed using light scattering results and MCT.

Experimental apparatus

Viscosity Apparatus: A Brookfield Viscometer Model DV-I+ with UL adapter is used to measure

the dynamic shear viscosity. It consists of a set of seven spindles (RV SPINDLE SET) with accuracy $\pm 1\%$. The spindles measure viscosity range from 1 up to 13300000 cP. UL adapter is used to make accurate and reproducible measurements with low viscosity. It is usually operated with spindle number 0 at 60 RPM^[12].

Temperature Controller: Julabo F25-MV Refrigerated and Heating Circulator with accuracy $\pm 1\%$ is used to control the temperature of the sample in the UL adapter^[18].

RESULTS AND DISCUSSION

Dynamic shear viscosity results

TABLE 1: The measured dynamic shear viscosity values as a function of temperature for different concentrations of carbon tetrachloride

x_{CCl4}	1	0.9	0.777	0.74	0.732	0.723	0.7	0.6	0.5	0.3	0
T(°C)	η (cP)										
20.00	1.07	1.69	2.37	2.94	3.20	3.31	3.80	7.10	11.50	23.40	56.00
21.00	1.06	1.66	2.30	2.88	3.14	3.20	3.73	7.00	11.10	22.50	55.00
21.50	1.05	1.61	2.24	2.84	3.10	3.10	3.69	6.83	10.90	22.20	54.00
22.25	1.03	1.57	2.20	2.77	3.15	3.04	3.63	6.61	10.60	21.40	52.00
23.00	1.02	1.54	2.18	2.70	2.94	2.97	3.52	6.55	10.20	20.90	51.50
24.00	1.00	1.50	2.16	2.65	2.84	2.93	3.41	6.45	9.71	20.30	48.00
25.00	0.99	1.49	2.13	2.56	2.77	2.85	3.31	6.35	9.45	19.30	46.00
27.00	0.97	1.39	2.03	2.45	2.58	2.64	3.09	6.00	8.70	17.10	40.60
30.00	0.96	1.28	1.81	2.10	2.40	2.45	2.80	5.23	7.85	15.80	32.70
35.00	0.91	1.17	1.60	1.92	2.05	2.08	2.45	4.83	6.72	12.90	25.30
40.00	0.85	1.07	1.30	1.65	1.76	1.86	2.24	4.37	6.08	11.00	19.00

TABLE 2 : The reciprocal of the absolute temperature and the logarithm of the dynamic shear viscosity of the system at the concentration extremes

T (K)	$\frac{1}{T} (K^{-1}) * 10^{-3}$	$\eta_{(x_{CCl4} = 0)}$ (cP)	Log $\eta_{(0)}$	$\eta_{(x_{CCl4} = 1)}$ (cP)	Log $\eta_{(1)}$
293.15	3.41	56.00	1.74819	1.07	0.02940
294.15	3.40	55.00	1.74036	1.06	0.02530
294.65	3.39	54.00	1.73239	1.05	0.02119
295.40	3.38	52.00	1.71600	1.03	0.01284
296.15	3.37	51.50	1.71180	1.02	0.00860
297.15	3.36	48.00	1.68124	1.00	0.00000
298.15	3.35	46.00	1.66276	0.99	-0.00440
300.15	3.33	40.60	1.60853	0.97	-0.01320
303.15	3.29	32.70	1.51455	0.96	-0.01800
308.15	3.24	25.30	1.40312	0.91	-0.04100
313.15	3.19	19.00	1.27875	0.85	-0.07060

The results of the dynamic shear viscosity η as a function of temperature for different concentrations of carbon tetrachloride are given in TABLE 1.

TABLE 1 shows that at each concentration of carbon tetrachloride, the viscosity decreases as the temperature increases, because when heat is applied to liquids, the molecules can then slide over each other more easily making the liquid to become less viscous. And for each temperature, the viscosity increases as the concentration of carbon tetrachloride x_{CCl4} decreases from 1 to 0, because coconut oil substance is more viscous than carbon tetrachloride.

Viscosity of pure components

The dynamic shear viscosities of the concentra-

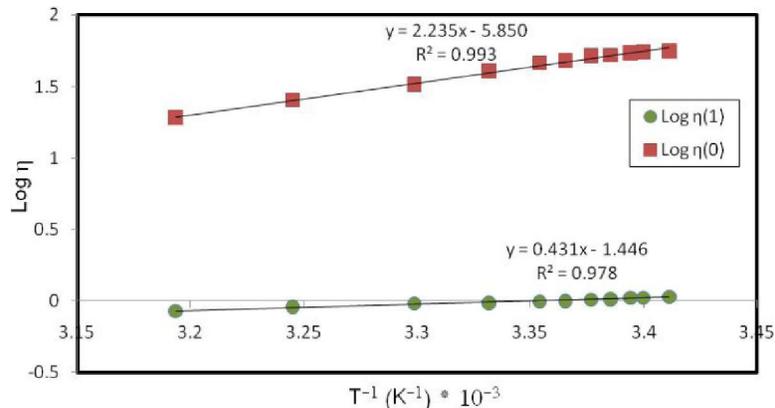


Figure 1: The logarithm of the dynamic shear viscosity versus the reciprocal of the absolute temperature for $x_{\text{CCl}_4} = 0, 1$

TABLE 3 : The values of the constants B and C for the two pure liquids CCl_4 and coconut oil from literatures and from this work

Constant	Literature values		This work	
	CCl_4 (Dutt and Prasad; 2004)	Coconut oil (Mesquita <i>et al</i> ; 2012)	CCl_4	Coconut oil
B	541.88	1908.19	431.62	2235.20
C	-1.86	-5.17	-1.45	-5.85

tions ($x_{\text{CCl}_4} = 0, 1$) is given in TABLE 2. The logarithm of the dynamic shear viscosity for these concentrations and the inverse absolute temperatures are calculated.

The logarithm of the dynamic viscosity for the concentrations ($x_{\text{CCl}_4} = 0, 1$) is plotted versus the reciprocal of the absolute temperature in Figure 1.

Figure 1 shows a linear relation between $\log \eta$ and T^{-1} for the pure components with the equations:

$$\text{Log } \eta = \frac{2235.2}{T} - 5.8506 \text{ for coconut oil}$$

and

$$\text{Log } \eta = \frac{431.62}{T} - 1.4467 \text{ for } \text{CCl}_4$$

The pure components viscosity equations can be fitted to Eq.(1). The value of C gives the logarithm of the shear viscosity of the given liquid when T approaches infinity.

TABLE 3 shows our values of B and C for CCl_4 and coconut oil compared with the literature values, they are in good agreement with each other.

Shear viscosity anomaly near the critical point

The critical point of the binary mixture CCl_4 -coconut oil was determined by Battacharya and Deo. The critical temperature T_c is 22.2 °C and the criti-

cal concentration x_c is 0.732 by weight of carbon tetrachloride^[11].

The viscosity values in TABLE 1 are plotted as a function of concentration of CCl_4 for different temperatures in Figure 2.

The dynamic shear viscosity behaves anomalously near the concentration 0.732 by weight of carbon tetrachloride and the temperature 22.20 C, this gives an indication that this is the critical point ($T_c = 22.20$, $x_c = 0.732$ by weight of CCl_4) for the binary mixture CCl_4 -coconut oil, which is in good agreement with the literature value.

The anomalous behavior starts from temperatures nearly 8 °C above the critical temperature $T_c = 22.20$ °C and 2 °C below it, and the amplitude of the viscosity anomaly increases as the temperature approaches the critical temperature.

Kinematic viscosity anomalous behavior

The kinematic viscosity ν (cSt) at the critical concentration of the binary mixture is calculated for different temperatures in TABLE 4. The behavior of the kinematic and the dynamic shear viscosity at the critical concentration $x_{\text{CCl}_4} = 0.732$ near the critical temperature 22.20 °C is shown in Figure 3.

Kinematic shear viscosity shows anomalous be-

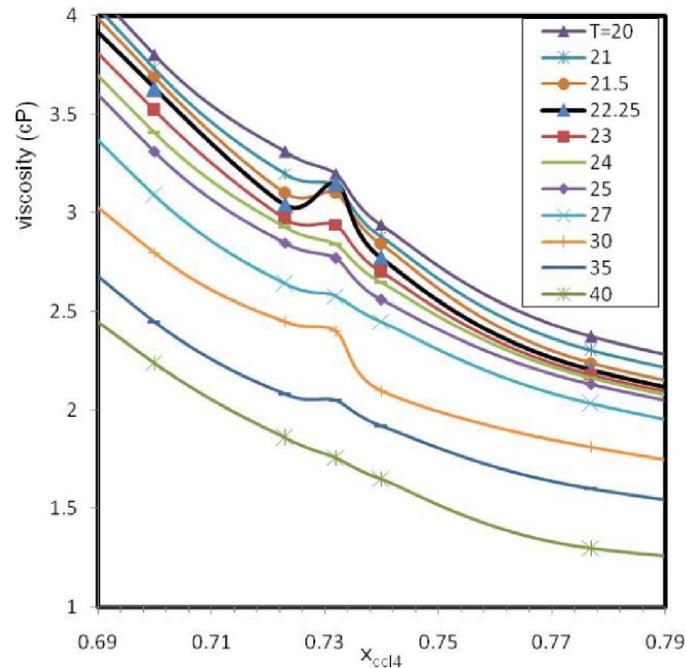


Figure 2 : The measured values of shear viscosity versus concentration of carbon tetrachloride for different temperatures

TABLE 4 : The measured dynamic shear viscosity and density values at the critical concentration are used to determine the kinematic viscosity behavior near the critical temperature

T (°C)	η_c (cP)	ρ (gm/ml)	ν_c (cSt)
20.00	3.20	1.217	2.63
21.00	3.14	1.214	2.59
21.50	3.10	1.213	2.56
22.25	3.15	1.207	2.61
23.00	2.94	1.203	2.44
24.00	2.84	1.200	2.37

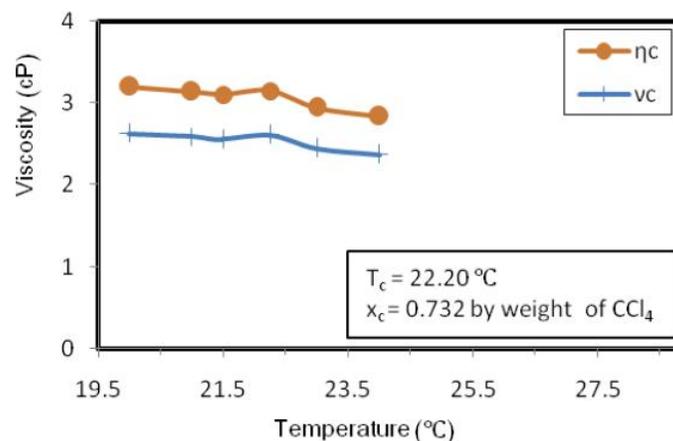


Figure 3 : The anomalous behavior of the dynamic and the kinematic shear viscosity at the critical concentration near the critical temperature

havior near the critical point with the value 2.61 cSt at the critical point, a value that is lower than the dynamic shear viscosity value at that point which is

equal to 3.15 cP.

Application of the MCT approach

MCT of the dynamic shear viscosity of Perl and

Full Paper

TABLE 5 : The measured values of dynamic shear viscosity at the critical concentration slightly above the critical temperature and the value of $\tau^{-0.04}$

T (°C)	T (K)	τ	$\tau^{-0.04}$	η (cP)
22.25	295.40	0.0002	1.42	3.15
23.00	296.15	0.0027	1.27	2.94
24.00	297.15	0.0061	1.23	2.84
25.00	298.15	0.0095	1.20	2.77
27.00	300.15	0.0163	1.18	2.58
30.00	303.15	0.0264	1.16	2.40

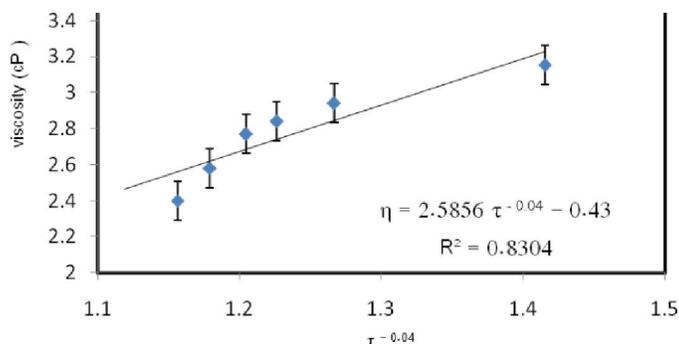


Figure 4 : The measured dynamic shear viscosity at the critical concentration near the critical temperature versus $\tau^{-0.04}$.

Ferrell and Kawasaki is applied at the critical concentration slightly above the critical temperature in order to determine the background viscosity η_0 , the MCT constant A and the upper cutoff wave number q_D .

The background viscosity η_0

The data of dynamic shear viscosity coefficients η at the critical concentration above the critical temperature $0.05 \leq T - T_c \leq 8$ °C are given in TABLE 5 and the value of $\tau^{-0.04}$ for each viscosity value is also calculated.

The measured dynamic shear viscosity η at the critical concentration is plotted versus $\tau^{-0.04}$ as shown in Figure 4.

It gives a linear relation which can be compared to Eq.(6) to observe that the slope is equal to the background viscosity η_0 . A least square fit gives the best value for η_0 , which is equal to 2.59 cP.

Our value of η_0 is in good agreement with the literature value which is equal to 2.59 cP^[9].

The MCT Constant A

The value of A can be determined using Perl and Ferrell logarithmically diverging viscosity law near the critical point Eq.(7); which can be written as:

$$\frac{\Delta\eta}{\eta} = \frac{(\eta - \eta_0)}{\eta} = A \ln q_D + A \ln \xi \quad (8)$$

is calculated in the previous section to be 2.59 cP, and the value of ξ_0 was calculated for our system to be 1.1 Å^[9], and it will be used to determine the values of ξ using Eq.(3).

The relative anomalous shear viscosity $\frac{\Delta\eta}{\eta}$ and the logarithm of the average correlation length $\ln \xi$ is calculated in TABLE 6 at the critical concentration and above the critical temperature.

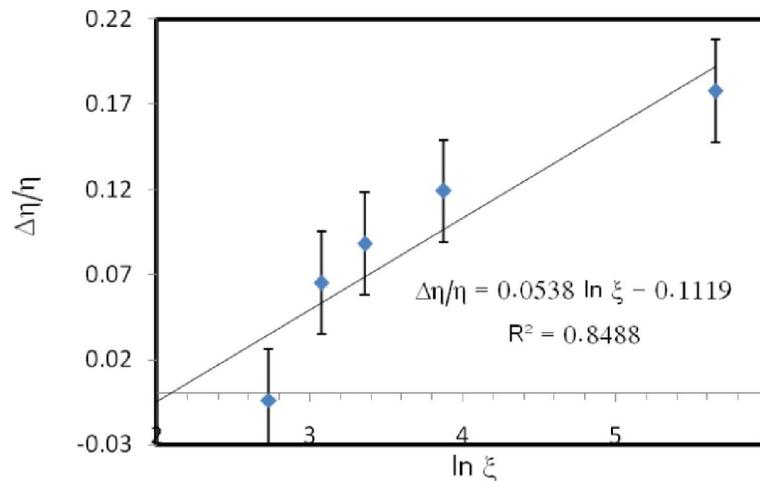
The behavior of the average correlation length ξ as a function of the reduced temperature τ is clearly observed in TABLE 6; as $T \rightarrow T_c$ the average correlation length becomes larger and larger, when the temperature reaches the critical temperature the correlation length diverges.

The relative anomalous shear viscosity $\frac{\Delta\eta}{\eta}$ is plotted versus the logarithm of the average correlation length $\ln \xi$ in Figure 5.

Figure 5 shows that the relation between $\frac{\Delta\eta}{\eta}$ and $\ln \xi$ is a linear relation with the slope equals to A

TABLE 6 : The anomalous shear viscosities at the critical concentration and the logarithm of the average correlation length

T (°C)	T (K)	τ	$\tau^{-0.64}$	Ξ	$\ln \xi$	η	$\Delta \eta/\eta$
22.25	295.40	0.0002	259.20	285.10	5.65	3.15	0.18
23.00	296.15	0.0027	43.96	48.35	3.88	2.94	0.12
24.00	297.15	0.0061	26.16	28.78	3.36	2.84	0.09
25.00	298.15	0.0095	19.72	21.69	3.08	2.77	0.06
27.00	300.15	0.0163	13.96	15.36	2.73	2.58	0.00

**Figure 5 :** The relative anomalous shear viscosity versus the logarithm of the average correlation length $\ln \xi$.**TABLE 7:** The measured and calculated values of A for different binary mixtures

Binary system	Calculated A	Measured A	Reference
Aniline-cyclohexane	0.054	0.056	(D'Arrigo <i>et al</i> ; 1977)
Triethylamine-water		0.054	(Swinny and Henry; 1973)
CCl ₄ -coconut oil		0.0538	This work

value which is 0.0538.

The measured and calculated values of the constant A for different binary mixtures are given in TABLE 7.

The measured value of A in our work is in good agreement with the literature values, and it is independent of the type of the binary mixture.

Debye momentum cutoff q_D

The upper cutoff wave number q_D , which is a free parameter in MCT, can be found from the intercept of Figure 5 and the value of the MCT constant A. Using of Eq.(8) the value of q_D is 0.126 \AA^{-1} . Determining q_D of the binary mixture CCl₄ and coconut oil supports the MCT of the critical viscosity.

Debye parameter L

The intermolecular force range or Debye parameter L can be calculated from light scattering results.

A relation between the correlation length and the intermolecular force range is given in Eq.(5): ($L = 2.45 \xi_0 T_c^{\frac{(\gamma-1)}{2}}$); T_c is 295.35 K and ξ_0 is 1.1 \AA for the binary mixture CCl₄- coconut oil. Substituting the values of ξ_0 , T_c , and γ in Eq.(5), the value of Debye parameter is 5.5 \AA .

The long range value of L indicates that the mutual forces between different molecules, in the binary mixture CCl₄-coconut oil, can be considered as a weak attractive force.

CONCLUSION

Dynamic shear viscosity behaves anomalously near the critical point, the anomalous behavior is explained theoretically using MCT.

The values of the background viscosity η_0 , the Debye momentum cutoff q_D , and the Debye param-

Full Paper

eter L were determined for the binary mixture CCl_4 and coconut oil, they are fluid dependent constants. The MCT constant A which is fluid independent, was evaluated, its value is consistent with the theoretical value.

Shear viscosity coefficients and other information about the binary mixtures are important for the scientists working on the improvement of molecular theories.

REFERENCES

- [1] I.Abdelraziq; "Concentration and temperature dependence of shear viscosity of the critical mixture of nitroethane and 3-methylpentane", *An-Najah Univ.J.Res.(N.Sc)*, **16**, 117-124 (2002).
- [2] I.Abdelraziq; "Critical amplitude of acoustical attenuation in mode-coupling theory for the binary mixture aniline and cyclohexane", *An-Najah Univ.J.Res.*, **15**, 11-20 (2001).
- [3] I.Abdelraziq; "Critical behavior of the ultrasonic attenuation for the binary mixtures of benzene-coconut oil and hexane— β , β -dichloroethylene ether", *Acta.Acoustica united with Acustica*, **91**, 716-722 (2005).
- [4] I.Abdelraziq; "The behavior of the ultrasonic of the cyclohexane and aniline", *Islamic Univ.J.*, **4**, (1996).
- [5] I.Abdelraziq; "Two-scale-factor universality of binary liquid critical mixtures", *Pakistan Journal of Applied Science*, **3**, 142-144 (2003).
- [6] I.Abdelraziq; "Ultrasonic absorption in critical binary mixture of perfluoromethylcyclohexane and carbon tetrachloride", *J.Acoust.Soc.Am.*, **107**, 788-792 (2000).
- [7] I.Abdelraziq, Esquivel R.Sirvent, S.S.Yun, B.Tan, F.B.Stumpf; "Absorption and velocity of ultrasound in binary solutions of poly(ethylene glycol) and water", *J.Acoust.Soc.Am.*, **93**, 819-820 (1993).
- [8] I.Abdelraziq, S.Musameh, Abu-Jafar; "Shear viscosity anomaly near the critical binary system of nitrobenzene-n-heptane", *Bethlehem Univ.J.*, **16**, (1996).
- [9] I.Abdelraziq, S.S.Yun, F.B.Stumpf; "Critical behavior of the ultrasonic attenuation and velocity and shear viscosity for the binary mixture of carbon tetrachloride and coconut oil", *J.Acoust.Soc.Am.*, **91**, 844-848 (1992).
- [10] I.Abdelraziq, S.S.Yun, F.B.Stumpf; "Critical behavior of the ultrasonic attenuation and velocity and shear viscosity for the binary mixture of nitrobenzene-N-hexane", *J.Acoust.Soc.Am.*, **88**, 1831-1836 (1990).
- [11] A.C.Bhattacharya, B.B.Deo; "Ultrasonic propagation in multi-component system in the critical region", *Pramana*, **21**, 273-282 (1983).
- [12] Brookfield Engineering Laboratories, Inc., Middlebore, USA, manual no.M/92-021-K1098, (1999).
- [13] R.F.Chang, P.H.Keyes, J.V.Sengers, Alley; "Dynamics of concentration fluctuations near the critical mixing point of a binary fluid", *Phys.Rev.Lett.*, **27**, 1706 (1971).
- [14] G.D'Arrigo, L.Mistura, P.Tartagila; "Concentration and temperature dependence of viscosity in the critical mixing region aniline-cyclohexane", *J.Chem.Phys.*, **66**, 80 (1977).
- [15] P.Debye; "Angular dissymmetry of the critical opalescence in liquid mixtures", *J.Chem.Phys.*, **31**, 680 (1959).
- [16] C.R.Duhne; "Viscosity-temperature correlations for liquids", *Chem.Eng.*, **86**, 83 (1979).
- [17] N.V.K.Dutt, D.H.L.Prasad; "Representation of the temperature dependence of the viscosity of pure liquids", Private Communication, Chemical Engineering Division, Indian Institute of Chemical Technology, Hyderabad (2004).
- [18] Julabo MV controller manual ENG, manual no.1.951.1402BE2 01/03, (2003).
- [19] K.Kawasaki; "High-frequency sound attenuation and dispersion in the critical region", *Phys.Rev.*, 1079 (1971).
- [20] K.Kawasaki; "Phase transitions and critical phenomena", Edited by Domb and Green (Academic, New York), **5A**, 165 (1976).
- [21] H.Klein, D.Woermann; "Analysis of light-scattering and specific heat data of binary liquid mixtures in terms of the two-scale-factor universality", *J.Phys.Chem.*, **82**, 1084-1086 (1978).
- [22] F.M.R.Mesquita, F.X.Feitosa, F.R.Do Carmo, R.S.De Santiago-Aguiar, H.B.De Sant'Ana; "Viscosities and viscosity deviations of binary mixtures of biodiesel + petrodiesel (or n-hexadecane) at different temperatures", *Brazilian Journal of Chemical Engineering*, **29**, 653-664 (2012).
- [23] R.Perl, R.A.Ferrell; "Decoupled-mode theory of critical viscosity and diffusion in the binary-liquid phase transition", *Phys.Rev.*, 2358-2369 (1972).
- [24] W.J.Popiel; "Laboratory Manual of Physical Chemistry", (1964).
- [25] H.L.Swinney, D.L.Henry; "Dynamics of fluids near the critical point: decay rate of order-parameter fluctuations", *Phys.Rev.*, 2586 (1973).
- [26] D.S.Viswanath, T.K.Ghosh, D.H.L.Prasad, N.V.K.Dutt, K.Y.Rani; "Viscosity of liquids, Theory, Estimation, Experiment and Data", 12-14 (2007).