

Debye Momentum Cutoff of the Critical Binary Mixture of Carbon Tetrachloride and Coconut Oil

Yusur. H. Kittany and Issam. R. Abdelraziq

Department of Physics, AN-Najah National University, Nablus 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 $T_c = 22.2$ °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 $L = 5.5$ Å. Mode Coupling Theory (MCT) of the dynamic shear viscosity is used to fit our experimental data above the critical temperature in the range $0.05 < T - T_c < 8$ °C. It is found that the noncritical part of the dynamic shear viscosity (background viscosity) $\eta_0 = 2.59$ cP and the Debye momentum cutoff (the upper cutoff wave number) $q_D = 0.126$ Å⁻¹. The MCT universal constant A is measured to be $A = 0.054$ which is consistent with the theoretical value.

1. Introduction

1.1 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 (Duhne; 1979):

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

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 (Viswanath *et al*; 2007):

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

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

1.2 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 (Popiel; 1964), 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 transition 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.

1.2.1 Light Scattering Results:

Light scattering experiment was used by Debye to study the critical binary mixtures. The correlation length, 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 (Debye; 1959, Chang *et al*; 1971):

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

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 (D'Arrigo *et al*; 1977, Klein and Woermann; 1978). 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 and the intermolecular force range L of the following form should exist (Debye; 1959):

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

Klein and Woermann show that the modified form of Eq.(4) is (Klein and Woermann; 1978):

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

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.

1.2.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 near the critical point can be written as a power law (Kawasaki; 1976, 1971):

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

Where, T^* is the reduced absolute temperature, η_0 is the noncritical part of the dynamic shear viscosity in cP, and ν_x is the critical exponent for the viscosity anomaly and it is equal to 0.04 (Klein and Woermann; 1978, Abdelraziq; 2002) .

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

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

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 $0.054 = \frac{8}{15\pi^2}$ (Kawasaki; 1976), 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 .

2. Experimental

2.1 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.

2.2 Experimental Apparatus:

Viscosity Apparatus: A Brookfield Viscometer Model DV-1+ 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 0.01 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 (Brookfield; 1999).

Temperature Controller: Julabo F25–MV Refrigerated and Heating Circulator with accuracy ± 1 % is used to control the temperature of the sample in the UL adapter (Julabo; 2003).

3. Results and Discussion:

3.1 Dynamic Shear Viscosity Results:

The results of the dynamic shear viscosity as a function of temperature for different concentrations of carbon tetrachloride are given in Table 3.1.

Table 3.1: The measured dynamic shear viscosity values as a function of temperature for different concentrations of carbon tetrachloride

x_{CCl_4}	1	0.9	0.777	0.74	0.732	0.723	0.7	0.6	0.5	0.3	0
T(°C)	(cP)										
20.0	1.07	1.69	2.37	2.94	3.20	3.31	3.80	7.10	11.50	23.40	56.00
21.0	1.06	1.66	2.30	2.88	3.14	3.20	3.73	7.00	11.10	22.50	55.00
21.5	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
23.0	1.02	1.54	2.18	2.70	2.94	2.97	3.52	6.55	10.20	20.90	51.50
24.0	1.00	1.50	2.16	2.65	2.84	2.93	3.41	6.45	9.71	20.30	48.00
25.0	0.99	1.49	2.13	2.56	2.77	2.85	3.31	6.35	9.45	19.30	46.00
27.0	0.97	1.39	2.03	2.45	2.58	2.64	3.09	6.00	8.70	17.10	40.60
30.0	0.96	1.28	1.81	2.10	2.40	2.45	2.80	5.23	7.85	15.80	32.70
35.0	0.91	1.17	1.60	1.92	2.05	2.08	2.45	4.83	6.72	12.90	25.30
40.0	0.85	1.07	1.30	1.65	1.76	1.86	2.24	4.37	6.08	11.00	19.00

Table 3.1 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. The viscosity increases as the concentration of carbon tetrachloride x_{ccl_4} decreases from 1 to 0, because coconut oil substance is more viscous than carbon tetrachloride.

3.1.1 Viscosity of Pure Components:

The dynamic shear viscosities of the concentrations ($x_{\text{CCl}_4} = 0, 1$) is given in Table 3.2. The logarithm of the dynamic shear viscosity for these concentrations and the inverse absolute temperatures are calculated.

Table 3.2: The reciprocal of the absolute temperature and the logarithm of the dynamic shear viscosity of the system at the extremes concentration

T (K)	$\frac{1}{T} \text{ (K}^{-1}) * 10^{-3}$	($x_{\text{CCl}_4} = 0$) (cP)	Log $\eta_{(0)}$	($x_{\text{CCl}_4} = 1$) (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 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 3.1.

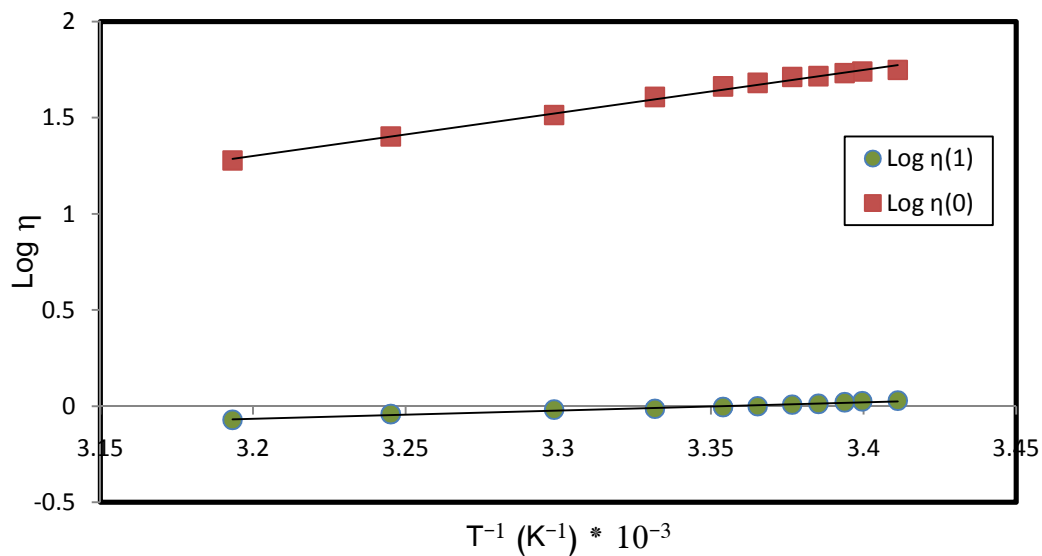


Figure 3.1: The logarithm of the dynamic shear viscosity versus the reciprocal of the absolute temperature for $x_{\text{CCl}_4} = 0, 1$.

Figure 3.1 shows a linear relation between $\log \eta$ and T^{-1} for the pure components with the equations:

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

and

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

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 3.3 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.

Table 3.3: 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

3.1.2 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 critical concentration x_c is 0.732 by weight of carbon tetrachloride (Battacharya and Deo; 1983).

The viscosity values in Table 3.1 are plotted as a function of concentration of CCl_4 for different temperatures in Figure 3.2.

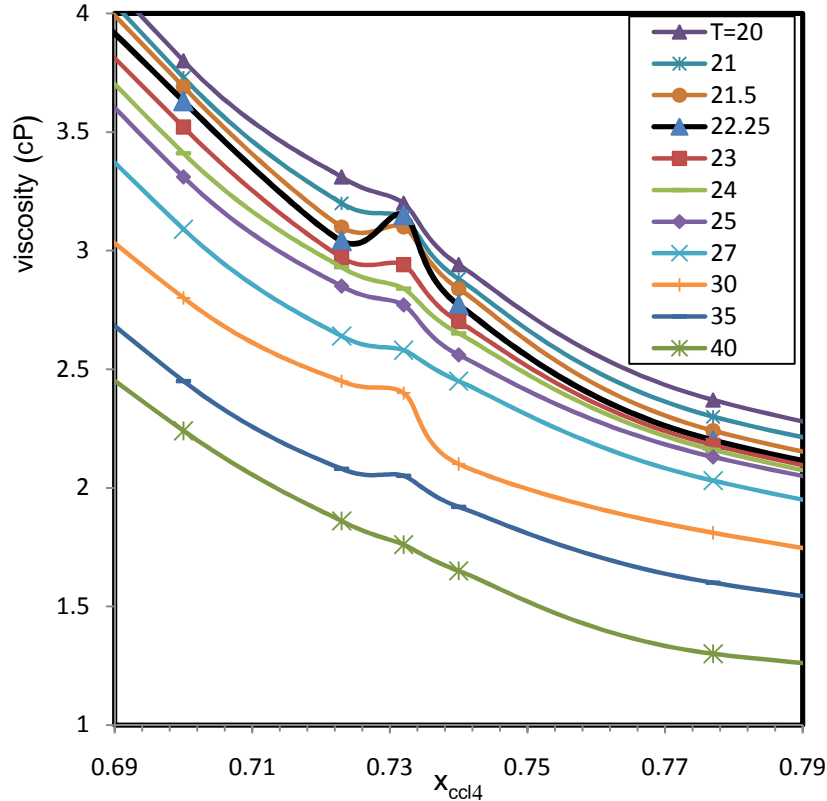


Figure 3.2: The measured values of shear viscosity versus concentration of carbon tetrachloride for different temperatures

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 amplitude of the viscosity anomaly increases as the temperature approaches the critical temperature.

3.1.3 Kinematic Viscosity Anomalous Behavior:

The kinematic viscosity ν (cSt) at the critical concentration of the binary mixture is calculated for different temperatures in Table 3.4. 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 3.3.

Table 3.4: 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)	(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

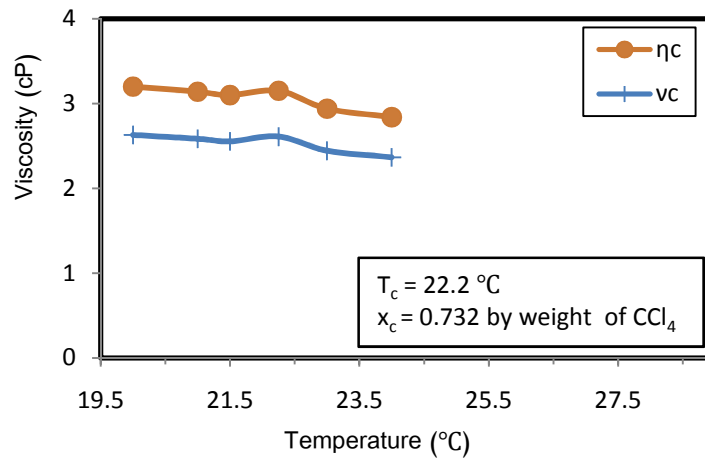


Figure 3.3: The anomalous behavior of the dynamic and the kinematic shear viscosity at the critical concentration near the critical temperature.

Kinematic shear viscosity shows anomalous behavior 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.

3.2 Application of the MCT Approach:

MCT of the dynamic shear viscosity of Perl and 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 .

3.2.1 The Background Viscosity η_0 :

The data of dynamic shear viscosity coefficients at the critical concentration above the critical temperature $0.05 \leq T - T_c \leq 8 \text{ }^\circ\text{C}$ are given in Table 3.5 and the value of $\tau^{-0.04}$ for each viscosity value is also calculated.

Table 3.5: The measured values of dynamic shear viscosity at the critical concentration and above the critical temperature

T (°C)	T (K)	τ	$\tau^{-0.04}$	(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

The measured dynamic shear viscosity η at the critical concentration is plotted versus $\tau^{-0.04}$ as shown in Figure 3.4.

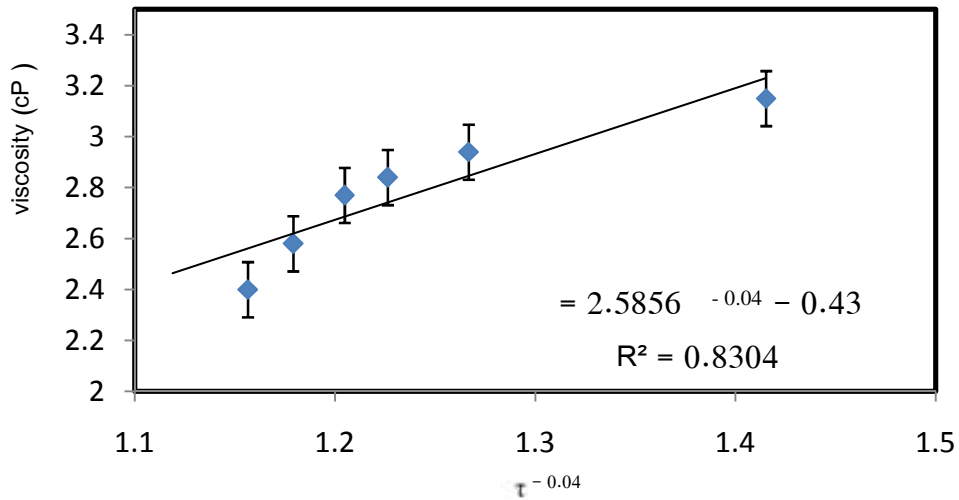


Figure 3.4: The measured dynamic shear viscosity at the critical concentration near the critical temperature versus $\tau^{-0.04}$

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 (Abdelraziq *et al*; 1992).

3.2.2 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:

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

η_0 is calculated to be 2.59 cP, and the value of q_D was calculated for our system to be 1.1 Å (Abdelraziq *et al*; 1992), and it will be used to determine the values of using Eq.(3).

The relative anomalous shear viscosity $\frac{\Delta\eta}{\eta}$ and the logarithm of the average correlation length \ln is calculated in Table 3.6 at the critical concentration and above the critical temperature.

Table 3.6: The anomalous shear viscosities at the critical concentration and the logarithm of the average correlation length

T (°C)	T (K)	$\frac{\Delta\eta}{\eta}$	$\frac{\Delta\eta}{\eta} \times 10^{-0.64}$	\ln	$\Delta /$	$\Delta /$	$\Delta /$
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

The behavior of the average correlation length as a function of the reduced temperature τ is clearly observed in Table 3.6; 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 3.5.

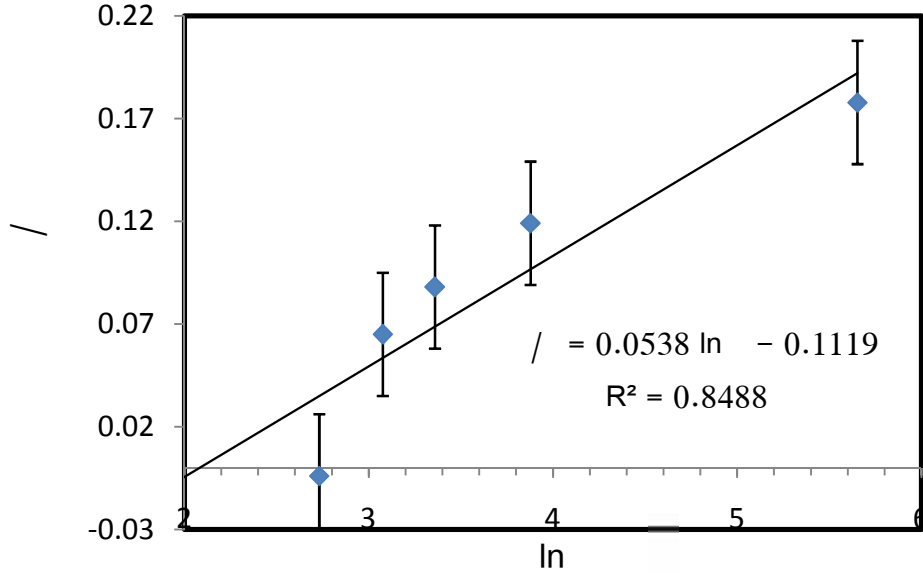


Figure 3.5: The relative anomalous shear viscosity $\frac{\Delta\eta}{\eta}$ versus the logarithm of the average correlation length $\ln \xi$.

Figure 3.5 shows that the relation between $\frac{\Delta\eta}{\eta}$ and $\ln \xi$ is a linear relation with the slope equals to A value which is 0.0538.

The measured and calculated values of the constant A for different binary mixtures are given in Table 3.7.

Table 3.7: 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

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.

3.2.3 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 3.5 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 CCl_4 and coconut oil supports the MCT of the critical viscosity.

3.3 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): $(L = 2.45 \eta_0 T_c^{\frac{(-1)}{2}})$; T_c is 295.35 K and η_0 is 1.1 \AA for the binary mixture CCl_4 -coconut oil. Substituting the values of η_0 , T_c , and L 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 CCl_4 -coconut oil, can be considered as a weak attractive force.

4. 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 parameter 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.

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