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## Critical behavior of refractive index of binary mixture cyclohexane – phenol

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### ABSTRACT

The dynamic viscosity of binary mixture of cyclohexane - phenol was measured over the entire range of temperatures and at concentration range (0.00% – 39.70%) by weight of phenol. The results above the critical temperature and critical concentration were analyzed by the mode coupling theory of one phase. The anomaly of dynamic viscosity was detected as a function of temperature and concentration. Dynamic viscosity anomaly was clearly observed near the critical temperature  $T_c = 17.0\text{ }^\circ\text{C}$  and the critical concentration  $\chi_c = 2.70\%$  by weight of phenol. The value of noncritical part of refractive index was found to be  $n_{0D} = 1.4276$ . The universal critical exponent for refractive index  $\chi_n$  is also calculated to be 0.00156. The behavior of refractive index of cyclohexane - phenol obeys power law universality above the phase transition. The isobaric specific heat for the critical binary

mixture  $c_{pc}$  was found to be  $106.6 \frac{\text{J}}{\text{kg}} \cdot \text{K}$  using twoscale factor universality. Joule's constant for cyclohexane -

phenol binary mixture was found to be  $4.15 \frac{\text{Calorie}}{\text{J}}$ . © 2015 Trade Science Inc. - INDIA

### INTRODUCTION

Cyclohexane and phenol are two hazardous substances widely utilized in different industries. Therefore, the identification of their physico-chemical properties is highly crucial. Cyclohexane is a colorless organic solvent produced by reacting benzene with hydrogen. Cyclohexane is fractionated from petroleum and exists as a liquid at standard temperature and pressure (STP). It causes central nervous system depression as a result of acute exposures and may additionally cause irreversible damage to the liver and kidneys over prolonged exposure

The organic compound phenol is known as car-

bolic acid and phenic acid. It is a colorless white crystalline solid at room temperature and naturally available. Besides its uses in chemical laboratories, phenol is used in manufacturing plastics, fertilizers, paints, rubber, adhesives, and paper. Phenol and its vapors are corrosive and toxic to the eyes, the skin and the respiratory tract. It is very toxic to neurons and if injected into the blood stream it can lead to instant death by blocking the neural transmission system<sup>[3]</sup>.

### THE CRITICAL POINT

A critical point is the term coined when both temperature and concentration are stabilized at their

critical values. The two liquids behave as one liquid with new physical characteristics. The temperature and concentration at which the two liquids become completely miscible at all proportions are called critical temperature  $T_c$  and critical concentration  $\chi_c$ , respectively. A pure liquid has a critical point at the end of the vapor-liquid coexistence curve.

Many properties for different binary mixtures have been studied near their critical points, including the dynamic shear viscosity, bulk viscosity, thermal expansion coefficient, heat capacity at constant pressure and constant volume, ultrasonic propagation, sound attenuation, ultrasonic velocity, refractive index and other physical properties<sup>[9, 25]</sup>.

## REFRACTIVE INDEX

Refractive index of a given medium is a physical property for that medium. It is a dimensionless value which describes how light or any radiations can propagate through the medium.

Refractive index determines how much light is refracted. It can be defined as the ratio between the speed of light in vacuum and the speed of light in medium as expressed in equation (1):

$$n_D = \frac{c}{v} \quad (1)$$

Where  $n_D$  is the refractive index of the medium at wavelength 589.29 nm (The Fraunhofer D line),  $c$  is the speed of light in vacuum, and  $v$  is the speed of light in medium.

Refractive index is affected by factors such as density and temperature of the medium. The speed of electromagnetic waves (light) decreases for medium with high density causing a decrease in refractive index<sup>[4]</sup>. The refractive index is inversely proportional to the temperature<sup>[18]</sup>. In addition, it depends on the wavelength of the incident light<sup>[16]</sup>.

The refractive index is one of the most important physical properties of a transparent solid, liquid and gas. Accurate knowledge of refractive index is correlated to the concentration, temperature, wavelength and pressure for transparent fluids. It can be used for the identification and characterization of pure materials. Concentrations of multi-

component mixtures can be measured using values of refractive indices<sup>[23]</sup>.

To our knowledge, the physic-chemical properties of the cyclohexane-phenol binary mixture were not identified. Therefore, here we measured the viscosity of cyclohexane-phenol binary mixture as a function of temperature over the entire possible concentration range to determine the critical point. This was followed by the determination of the critical temperature and critical concentration of cyclohexane-phenol binary mixture. The data extrapolated will be employed in setting up the power law for the refractive index and calculating the critical exponent  $\chi_n$  of the critical binary mixture. The critical isobaric heat capacity for the mixture will also determine at the critical point. Finally, the Joule's constant for the binary mixture will be identified.

## THEORY

### Viscosity

Viscosity measures the resistance of a fluid to gradual deformation by shear stress or tensile stress. For liquids, it corresponds to the informal notion of "thickness". Viscosity is due to friction between neighboring particles of the fluid that are moving at different velocities<sup>[27]</sup>.

The shear viscosity of a fluid can be expressed in two distinct forms:

### The dynamic or absolute shear viscosity

The dynamic shear viscosity is defined as the ratio of shear stress (force over cross section area) to the rate of shear deformation or shear velocity.

$$\eta = \frac{\tau}{\frac{\partial y}{\partial x}} \quad (2)$$

Where  $\eta$  dynamic shear viscosity in (Pa.s) is,  $\tau$  is shear stress in (N/m<sup>2</sup>), and  $\frac{\partial y}{\partial x}$  is rate of deformation (shear rate) in (s<sup>-1</sup>)<sup>[8]</sup>.

The dynamic shear viscosity unit is the centipoise (cP).

### Kinematic viscosity

The kinematic viscosity is the dynamic viscosity  $\eta$  divided by the mass density of the fluid  $\rho$

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$$\nu = \frac{\eta}{\rho} \quad (3)$$

Where,  $\nu$  is kinematic viscosity in centistokes (cSt), and  $\rho$  is mass density<sup>[8]</sup>.

### Dynamic shear viscosity of pure liquids

The viscosity of a pure liquid is affected by temperature, pressure, density and surface tension of that liquid. The dynamic shear viscosity of liquids decreases with increasing temperature and decreasing pressure<sup>[8]</sup>.

Liquids have complex nature; therefore, several theories were proposed to describe the viscosity. Like the theoretical methods of calculating liquid viscosities, the molecular dynamic approaches, semi-empirical and empirical methods. The equation that explains the correlation between the dynamic viscosity and the temperature is in the form of an Arrhenius-type equation<sup>[6]</sup>.

$$\eta = \eta_0 e^{\frac{E_\eta}{RT}} \quad (4)$$

Where  $\eta$  is the measured dynamic shear viscosity in (cP),  $\eta_0$  is the dynamic shear viscosity at some reference temperature,  $E_\eta$  is the activation energy in (J/mol),  $R$  is the universal gas constant (J/mol.K) and  $T$  is the absolute temperature (K).

The logarithm of liquid viscosity varies linearly with the reciprocal of the absolute temperature  $T$  below the normal boiling point which is described by the empirical model.

$$\ln(\eta) = \bar{A} + \frac{B}{T} \quad (5)$$

Where  $\bar{A}$  and  $B$  are constants determined empirically.

At temperatures above the normal boiling point, the  $\ln(\eta)$  versus  $\frac{1}{T}$  relationship becomes nonlinear and is described by a number of semi empirical methods.

### Dynamic shear viscosity of mixtures

Viscosity is studied by several methods for solutions (homogeneous products of dissolution of solids or gases in liquids) and for liquid mixtures (homogeneous mixtures resulting from mixing of two or more liquids). Some of the methods are developed using excess Gibbs free energy models include Wil-

son, non-random two-liquid (NRTL) and universal quasi chemical (UNIQUAC)<sup>[8]</sup>.

Far from the critical point (under or above) of a binary liquid mixture, the behavior of the viscosity is like pure liquids, but around the critical point the situation becomes more complicated.

The mode coupling theory is used to study the critical anomaly of the dynamic shear viscosity and the coefficients.

### The mode coupling theory

The “mode” refers to eigenmodes of an idealized, “unperturbed”, linear system. The superposition principle indicates that eigenmodes of linear systems are independent of each other. In most real systems, there are at least some perturbations that cause energy transfer between different modes. This perturbation is interpreted as an interaction between the modes. Therefore, the term “mode coupling” is coined to describe this theory<sup>[13]</sup>.

Mode coupling theory is applied when the modes of one fluid are perturbed by the modes of the other fluid. Such perturbations lead to coupling and exchange of energy<sup>[19]</sup>, which indicates the start of the interaction between the fluids layers. It started originally by Fixman who proposed mechanisms by which the relaxation time and the kinetic coefficients, such as viscosity and density, could diverge at a critical point<sup>[9]</sup>. These ideas were more fully developed by Kawasaki, Kadanoff and Swift<sup>[15, 14]</sup>.

Reichman and Charbonneau derived the mode-coupling equations for the description of density fluctuations from microscopic considerations. In addition, they derived schematic mode-coupling equations of a similar form from a field-theoretical perspective. They reviewed the successes and failures of the mode-coupling theory, and discussed recent advances in the applications of the theory<sup>[24]</sup>.

The theories that describe the critical absorption of the binary mixture are based on the mode-coupling theory which considers the effect of two mode states. These theories are based on understanding fluctuations that occur in those binary mixtures rather than focusing on microscopic aspects<sup>[9]</sup>. The available theories can thus give important information about how binary mixtures act at their critical

points<sup>[10]</sup>.

Dynamic shear viscosity near the critical point:

The critical anomaly of the dynamic shear viscosity coefficient by Kawasaki and Perl and Ferrell is given according to the equation (6)<sup>[21]</sup>:

$$\frac{\eta - \eta_0}{\eta} = \frac{\Delta\eta}{\eta} = A \ln(\xi) + A \ln(q_D) \quad (6)$$

Where  $\eta$  is the noncritical part of the measured dynamic shear viscosity,  $\xi$  is the mode-coupling theory universal constant predicted to have the theoretical

value  $\frac{8}{15\pi^2} = 0.054$ <sup>[7]</sup>,  $\xi$  is the correlation length and  $q_D$  is the Debye momentum cutoff.

Mode coupling theory predicts a divergence of the kinetic coefficients near the critical point. One of the kinetic transport coefficients is the dynamic shear viscosity  $\eta$ . The divergence of  $\eta$  can be described near the critical point. However, 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 critical point. The dynamic shear viscosity  $\eta$  is temperature dependent at the critical concentration which is given by the power law equation (7):

$$\eta = \eta_0 t^{-\chi_{\eta\nu}} \quad (7)$$

Where  $t$  is the reduced temperature,  $\eta_0$  is the noncritical part of the dynamic shear viscosity in cP, and  $\chi_{\eta\nu}$  is the critical exponent for the dynamic shear viscosity anomaly which equals 0.04<sup>[17, 21]</sup>.

The correlation length is the average distance between two molecules at temperatures near the critical temperature. The correlation length expression is given by equation (8):

$$\xi = \xi_0 t^{-\nu} \quad (8)$$

This is related to the reduced temperature  $T_c$  near the critical temperature and critical concentration  $X_c$ .

Van der Waals intermolecular forces act between stable molecules or between functional groups of macromolecules. The intermolecular force range is the reciprocal of the correlation length  $\xi$  at  $\eta = \eta_0$ <sup>[5]</sup>.

The mode-coupling theory has important applications such as fiber optics, lasers, and condensed-matter physics, to describe the slowing down of the critical behavior.

## Refractive index of a binary mixture

The refractive index  $n_D$  of any mixture can be calculated from the knowledge of the refractive index and the mass density of pure components.  $n_D$  can be measured in all ranges of existing temperatures and can also be deduced theoretically<sup>[26]</sup>. The Lorentz and Lorenz mixing rule in the form reported have been verified for the system under investigation<sup>[28]</sup>. This rule was used to calculate the refractive index for the phenol-cyclohexane binary mixture theoretically. The rule is given by equation (9):

$$n_D = \sqrt{\frac{(2A + 1)}{(1A)}} \quad (9)$$

Where is given by equation (10):

$$A = \left\{ \left[ \frac{(n_{1D}^2 - 1)}{(n_{2D}^2 + 2)} \right] \frac{1}{\rho_c} - \left[ \frac{(n_{1D}^2 - 1)}{(n_{2D}^2 + 2)} \right] \frac{W_1}{\rho_1} + \left[ \frac{(n_{2D}^2 - 1)}{(n_{2D}^2 + 2)} \right] \frac{W_2}{\rho_2} \right\} \rho_c \quad (10)$$

Where  $n_{1D}$  and  $n_{2D}$  are the pure components refractive indices,  $W_1$  and  $W_2$  are the weight fractions,  $\rho_c$  is the mixture mass density at critical temperature and critical concentration,  $\rho_1$  and  $\rho_2$  are the pure components mass densities<sup>[20]</sup>.

## Power law of refractive index

Specific heat, thermal expansion coefficient and thermal conductivity and other thermodynamic properties, diverge as the critical temperature  $T_c$  is approached with the divergence obeying a power-law in  $|T - T_c|$ . Other thermodynamic properties show a non-divergent power-law. The exponents that go with these power laws are called critical exponents<sup>[22]</sup>.

The refractive index is expected to be temperature dependent, as viscosity and density of binary mixture, as given by the power law shown in equation (11):

$$n_D = n_{0D} t^{-\chi_{n\nu}} \quad (11)$$

Where  $t$  is reduced temperature, which is given by  $\frac{T - T_c}{T_c}$ ,  $\chi_{n\nu}$  is the universal critical exponent for the refractive index, and  $\nu$  is critical exponent which equals to 0.64<sup>[7, 17]</sup>.

## Two – scale – factor universality:

The two – scale – factor universality has been used in some theories to explain the critical phenomena of binary liquid mixtures by prediction of<sup>[11]</sup>. This quantity is defined in equation (12):

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$$R_{\xi} = \xi_0 \left( \left[ \frac{\alpha T_c \alpha_{pc}}{K_B T'_c} \right] \right)^{\frac{1}{d}} = \xi_0 \left( \left[ \frac{\alpha \rho_c c_{pc}}{K_B} \right] \right)^{\frac{1}{d}} \quad (12)$$

Where  $R_{\xi}$  is the universal quantity that equals 0.270<sup>[11]</sup>,  $\alpha$  is the critical exponent that equals 0.11,  $\rho_c$  is the mass density at the critical temperature,  $c_{pc}$  is the critical amplitude of the isobaric specific heat,  $K_B$  is the Boltzmann's constant,  $\alpha_{pc}$  is the critical amplitude of the thermal expansion and  $T'_c$  is the pressure derivation of the critical temperature along the critical line<sup>[1, 11]</sup>.

The specific heat at constant pressure  $c_p$  is given by the equation (13):

$$c_p = c_{pc} t^{-\alpha} + c_{pb} \quad (13)$$

Where  $c_{pc}$  is the critical amplitude of the isobaric specific heat that is calculated from equation (12) and  $c_{pb}$  is the background isobaric specific heat.

## METHODOLOGY

### The characteristics of the binary mixture components

#### Cyclohexane and phenol

Cyclohexane and phenol substances with purity (99.5%) were used in this work. The molecular structure of cyclohexane is shown in Figure (1).

Some physical and chemical properties for pure cyclohexane and pure phenol are given in TABLE (1).

#### Viscosity apparatus

A Glass capillary U-tube viscometer is used for

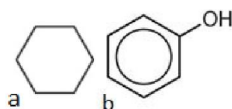


Figure 1 : The molecular structure of a) cyclohexane and b) phenol

TABLE 1 : Physical and chemical properties of cyclohexane and phenol

Property	Phenol (Lide, 1993)	Cyclohexane (Colette <i>et al</i> , 2003)
Molecular formula	C <sub>6</sub> H <sub>6</sub> O	C <sub>6</sub> H <sub>12</sub>
Molecular mass (gm/mol)	94.11	84.16
Boiling temperature (°C)	181.7	80.7
Melting temperature (°C)	43.0	6.5
Appearance	Transparent crystalline solid	Colorless liquid
Refractive index $n_D$ (at 20°C)	1.5425	1.4266
Density at (20°C) (gm/cm <sup>3</sup> )	1.0576	0.7792

viscosity measurement. It consists of a U-shaped glass tube held vertically in a controlled temperature bath. One of the U-tube arms is vertically oriented with a narrow bore that consists of two bulbs. The other arm has a large bulb lower down the two bulbs on the first arm.

#### Temperature controller

Julabo F25-MV Refrigerated and Heating Circulator with temperature range (-28 to 200 °C) of accuracy  $\pm 0.5$  is used to control the temperature of the sample in the glass capillary viscometer.

#### Digital thermometer

A digital thermometer with accuracy  $\pm 0.5\%$  is used to measure the temperature of the water path for the samples.

#### Refractive index apparatus

Digital abbe refractometer is used to measure the refractive indices ( $n_D$ ) of the samples with accuracy  $\pm 0.00005\%$  at the entire range of temperatures. Incident light with visible wavelength of D line wavelength (589.29 nm) is used.

#### Calorimeter

The specific heat of cyclohexane-phenol sample is measured using the calorimeter. Glass capillary viscometer, calorimeter cup and pycnometer are cleaned twice using ethanol alcohol (99.9%) and dried completely.

## SAMPLES PREPARATION

#### Density measurements

A volume of 10.0 ml is measured by a 10.0 ml pycnometer, and weighed using an HR-200 analyti-

cal balance with accuracy of  $\pm 0.00005\%$ .

### Concentration of samples

Samples of different concentrations are prepared in the range 0.00% to 39.70% by weight of phenol. The concentration of phenol in a given sample of cyclohexane and phenol in a given volume V can be calculated from equation (3.2):

$$\begin{aligned} X_{\text{phenol}} &= \frac{\text{mass of phenol}}{\text{total mass of the binary mixture}} \\ &= \frac{([\rho V]_{\text{phenol}})}{([\rho V]_{\text{phenol}} + [\rho V]_{\text{cyclohexane}}} \end{aligned} \quad (14)$$

The volume of phenol is changed to enable its addition to the sample. One component volume is fixed to find the volume of the other component for a specific concentration.

### Viscosity measurements

The sample of cyclohexane-phenol mixture is put into the upper bulb by suction. It is then allowed to flow down through the capillary into the lower bulb. Two marks (one above and one below the upper bulb) indicate a known volume. The time taken for the level of the liquid to pass between these marks is proportional to the dynamic shear viscosity. The time required for the test liquid to flow through a capillary of a known diameter of a certain factor between two marked points is measured. The experiment is performed three times for each concentration.

Viscosity of binary mixture can be calculated using equation (3.3):

$$\eta_{\text{mix}} = \frac{\eta_{\text{water}} t'_{\text{mix}} \rho_{\text{mix}}}{t'_{\text{water}} \rho_{\text{water}}} \quad (15)$$

Where  $\eta_{\text{mix}}$  the dynamic is shear viscosity of binary mixture;  $t'_{\text{mix}}$  is the time and  $\rho_{\text{mix}}$  is the mass density of binary mixture at certain temperature and concentration;  $\eta_{\text{water}}$  is the dynamic shear viscosity of water,  $t'_{\text{water}}$  is the time and  $\rho_{\text{water}}$  is the mass density of water at certain temperature.

Water viscosity at temperature range (0.0 °C – 20.0 °C) can be calculated using equation (3.4.1) (David. 1985):

$$\log \left[ \frac{\eta_T}{\eta_{20}} \right] = \frac{1301}{998.333 + 8.1855(T - 20) + 0.00583[(T - 20)]^2} - 1.30233 \quad (16)$$

Water viscosity at temperature range (20.0 °C – 100.0 °C) can be calculated using equation (3.4.2) (David, 1985):

$$\left[ \log \left( \frac{\eta_T}{\eta_{20}} \right) \right] = \frac{1.3272 (20 - T) - 0.001053 [(T - 20)]^2}{T + 105} \quad (17)$$

### Refractive index measurements

A sample of 20.0 ml of cyclohexane-phenol is incubated in a water bath until its temperature is equilibrated with the water bath. The temperature of the abbe refractometer prism is controlled using a thermo stated bath. Two drops of the sample are taken to measure  $n_D$  at certain temperature. Refractive indices are measured at temperature rang (14.0 – 12.0 °C).

### Isobaric specific heat measurement

The calorimeter is connected with the power supply, digital ammeter, and digital voltmeter. The 150.0 ml of critical binary mixture is weighted before being placed inside the calorimeter. The applied voltage is changed from power supply until the temperature 25.0 °C is reached for the binary mixture. The power supply is then cut off from the set and temperature started decreasing. The time needed to reach the certain temperature is measured using stopwatch.

The work done on the binary mixture is calculated using equation (3.5):

Work = current × volt × time

$$W = I \times V \times t' \quad (18)$$

Joule's constant (J) is calculated for cyclohexane-phenol mixture using equation (19):

$$J = \frac{H}{W} \quad (19)$$

Where H is the quantity of heat in calorie.

Heat quantity (H) can be calculated using equation (20):

$$H = (m_0 c_0 + m_s c_s + m_h c_h + m_{\text{mix}} c_p) \Delta T \quad (20)$$

Where:  $m_0$  is the mass of calorimeter cup (pyrex beaker),  $m_s$  is the mass of stirring rod,  $m_h$  is the mass of heater,  $m_{\text{mix}}$  is the mass of the binary mixture,  $c_0$  is the specific heat of calorimeter cup,  $c_s$  is the specific heat of stirring rod,  $c_h$  is the specific heat of heater and  $c_p$  is the specific heat of the binary mixture at critical concentration, and  $\Delta T$  is temperature difference.

## RESULTS

High-purity samples of cyclohexane and phenol were used in this work. The shear viscosities at temperatures ranging from 14.0 to 21.0 °C are measured for cyclohexane-phenol binary mixtures, over the entire composition range. The dependence of the shear viscosity on the concentration and temperature is determined. Refractive indices are measured at temperatures in the range 14.0 to 21.0 °C of different concentrations of cyclohexane - phenol binary mixture.

## Viscosity measurements

The dynamic viscosity values for cyclohexane-phenol mixture are measured for a concentration range (0.00% – 39.70%) by weight of phenol at temperature range (14.0 °C – 21.0 °C).

The dynamic shear viscosity of cyclohexane-phenol binary mixture depends on temperature. A positive relationship was found between the dynamic shear viscosity and the concentration of phenol in

the sample. This is due to the high viscosity of phenol in the mixture.

The dynamic shear viscosity of cyclohexane-phenol of different concentrations (0.00% - 39.70%) by weight of phenol is plotted as a function of temperature, as shown in Figures (1)–(4).

The dynamic shear viscosity behaves anomalously near the concentration 2.70% by weight of phenol and at the temperature 17.0 °C. This gives an indication that this is possibly the critical point ( $T_c = 17.0$  °C,  $\chi_c = 2.70\%$  by weight of phenol) for the binary mixture cyclohexane-phenol.

Figures (2) - (4) show that at each concentration of phenol the dynamic shear viscosity continuously decreases as the temperature increases. This is normal, because when temperature is applied to liquids the molecules their average kinetic energy increases. The molecules can then slide over each other more easily. The liquid thus becomes less viscous. Moreover, for each temperature the dynamic shear viscosity increases as the concentration of phenol increases because phenol substance is more viscous

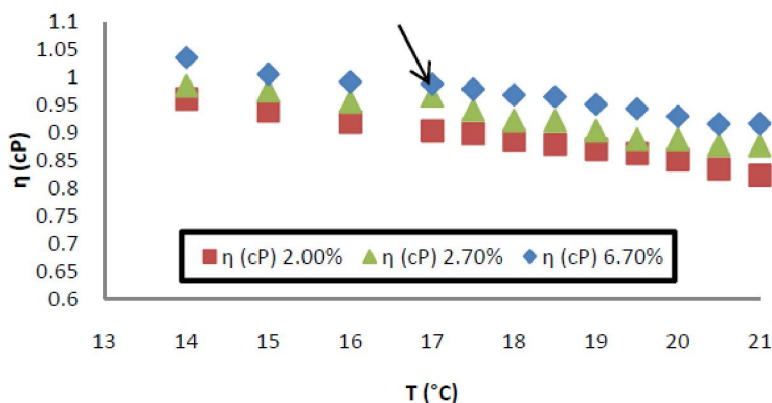


Figure 2 : Thedynamic shear viscosity of cyclohexane-phenol as a function of temperature of concentrations (2.00% - 6.70%) by weight of phenol

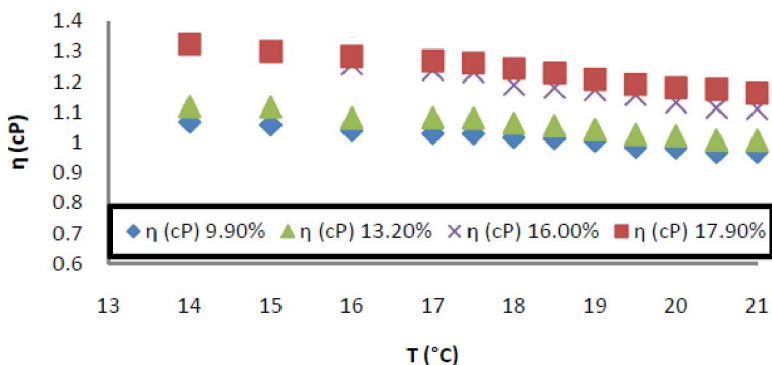


Figure 3 : Thedynamic shear viscosity of cyclohexane-phenol as a function of temperature of concentrations (9.90% - 17.90%) by weight of phenol

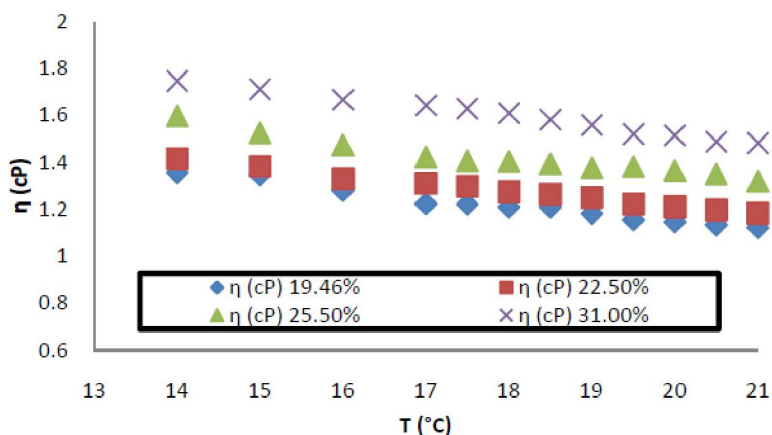


Figure 4 : The dynamic shear viscosity of cyclohexane-phenol as a function of temperature of concentrations (19.46% - 31.00%) by weight of phenol

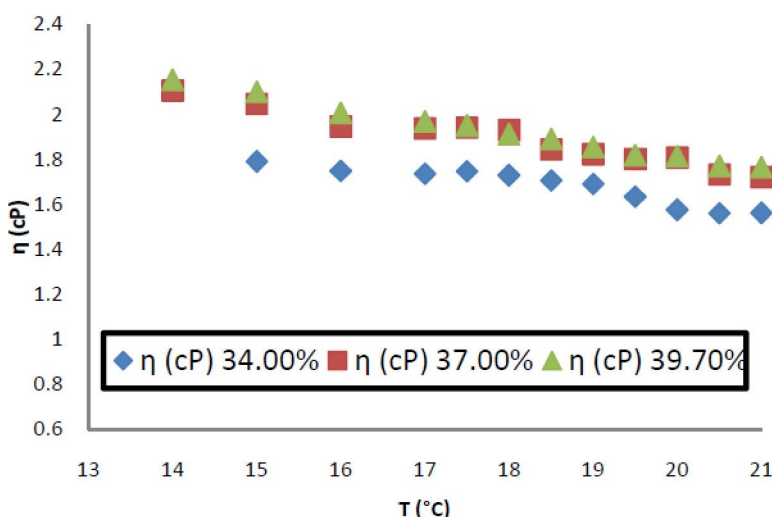


Figure 5 : The dynamic shear viscosity of cyclohexane-phenol as a function of temperature of concentrations (34.00% - 39.70%) by weight of phenol

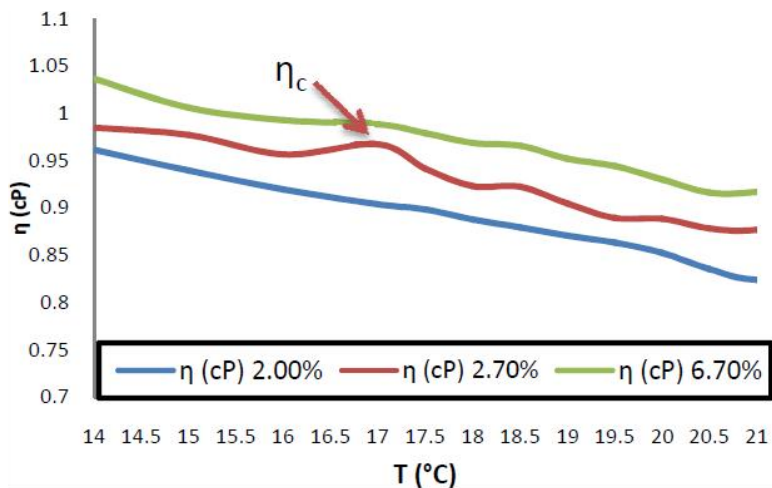


Figure 6 : Dynamic shear viscosity measured at different temperatures of 2.00%, 2.70% and 6.70% by weight of phenol

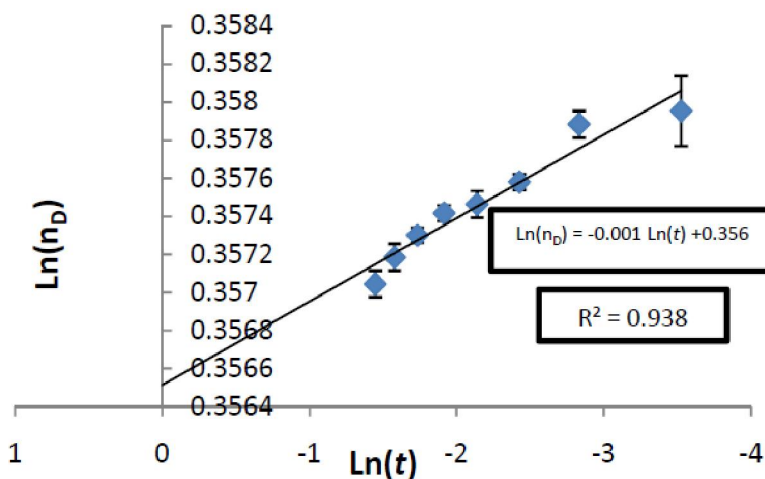
than cyclohexane. The viscosity dependence on the temperature at the critical concentration is different from the other concentrations; there are no anomalous behaviors for these concentrations.



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TABLE 2 : The measured refractive index values of critical binary mixture above critical temperature

$T$ (°C)	$T - T_c$	$t = \frac{T - T_c}{T_c}$	$n_D$	$\ln(n_D)$	$\ln(t)$
17.3	0.3	0.0176	1.431	0.3583	-4.0372
17.5	0.5	0.0294	1.4306	0.3580	-3.5264
18.0	1.0	0.0588	1.4304	0.3579	-2.8332
18.5	1.5	0.0882	1.4299	0.3576	-2.4277
19.0	2.0	0.1176	1.4297	0.3574	-2.1401
19.5	2.5	0.1470	1.4296	0.3573	-1.9169
20.0	3.0	0.1764	1.4295	0.3573	-1.7346
20.5	3.5	0.2058	1.4294	0.3572	-1.5805
21.0	4.0	0.2352	1.4292	0.3571	-1.4469

Figure 7 : Shows the relation between  $\ln(n_D)$  and  $\ln(t)$ 

The anomaly can be clearly noticed by plotting the dynamic shear viscosity vs. temperature for the concentrations 2.00%, 2.70% and 6.70% by weight of phenol, as shown in Figure (6).

Figures (1) through (5) show a cusp at concentration  $\chi_c = 2.70\%$  by weight of phenol and temperature  $T_c = 17.0^\circ\text{C}$ . This point is considered to be a critical point. Mode coupling theory for the dynamic shear viscosity is used to fit the data near the critical point.

### The noncritical part of refractive index ( $n_{0D}$ )

The Lorentz and Lorenz mixing rule can be used to verify the refractive index values for different binary mixtures. However, employing this rule for phenol is difficult to achieve for its solid state characteristic at room temperature.

The power law of the refractive index  $n_D$  is used to determine the background refractive index  $n_{0D}$ . It also shows the reliance of refractive index on the

temperature. The data of refractive indices are fitted in the power law equation  $n_D = n_{0D} t^{-\chi_n \nu}$ , where  $n_{0D}$  the noncritical part of its refractive index,  $\chi_n$  and  $\nu$  is critical exponents, and  $t$  is the reduced temperature  $\frac{T - T_c}{T_c}$ .

The measured refractive indices  $n_D$  of the critical concentration above the critical temperature are given in TABLE (2).

Equation (14) gives relation between refractive index as a function of temperature. It can be re-written as shown in equation (15).

$$n_D = n_{0D} t^{-\chi_n \nu} \quad (14)$$

$$\ln(n_D) = \ln(n_{0D}) - \chi_n \nu \ln(t) \quad (15)$$

Figure (7) shows a linear relation between  $\ln(n_D)$  and  $\ln(t)$  which can be noticed from equation (15). Therefore, the determination of the value of the critical exponent  $\chi_n$  and the noncritical part of refractive index  $n_{0D}$  is achieved. The values for

the slope equals to  $\chi_n \nu = 0.001$ , but as  $\nu = 0.64$ , the universal constant for refractive index  $\chi_n = 0.00156$ . The intercept value  $Ln(n_{0D}) = 0.356$  is also needed to calculate the background refractive index  $n_{0D} = 1.4276$ . A least square fit gives the best value for  $\chi_n$ .

**Calculation of specific heat**

The specific heat under constant pressure at the critical temperature is calculated using the two scale factor universality.

The universal constant is given by equation (16)

$$R_{\xi} = \xi_0 \left( \left[ \frac{\alpha T_c \alpha_{pc}}{K_B T_c} \right] \right)^{\frac{1}{d}} = \xi_0 \left( \left[ \frac{\alpha \rho_c c_{pc}}{K_B} \right] \right)^{\frac{1}{d}} = 0.270 \quad (16)$$

Where the critical exponent  $\alpha = 0.11$ , dimension  $d = 3$ , the mass density of binary mixture cyclohexan-phenol at the critical temperature  $\rho_c = 0.7627 \text{ gm/cm}^3$  that is found in this work, Boltzmann's constant is given by  $K_B = 1.38 \times 10^{-23} \text{ J/k}$ ,  $\xi_0$  is the noncritical part of correlation length for critical binary mixture and it is equal to  $3.12 \text{ \AA}^{[2]}$ . The value for  $c_{pc}$  can

be calculated to be  $106.6 \frac{\text{J}}{\text{kg}} \cdot \text{K}$ .

$$c_p = c_{pc} t^{-0.11} + c_{pb} \quad (17)$$

The isobaric specific heats  $c_p$  values can be cal-

culated at different temperatures close to the critical temperature ( $17.0 \text{ }^\circ\text{C}$ ) are given in TABLE (3).

The average value for is  $135.2 \frac{\text{J}}{\text{kg}} \cdot \text{K}$  for cyclohexane / phenol binary mixture.

**Joule's constant for cyclohexane-phenol binary mixture**

The specific heat at constant pressure of the critical cyclohexane/phenol binary mixture is calculated

to be  $135.2 \frac{\text{J}}{\text{kg}} \cdot \text{K}$ .

Joule's constant J for cyclohexane-phenol binary mixture can be calculated from equation (18):

$$J = \frac{H}{W} \quad (18)$$

Where H is heat quantity and it can be calculated from equation (19):

$$H = (m_0 c_0 + m_s c_s + m_h c_h + m_{mix} c_p) \Delta T \quad (19)$$

W is the work done on the binary mixture, it can be calculated from equation (20):

$$W = I \times V \times t \quad (20)$$

The values of different masses and different specific heats are given in TABLE (4):

Joule's constant values for different temperature

TABLE 3 : Isobaric specific heat data

T (°C)	$t = \frac{T - T_c}{T_c}$	$t^{-0.11}$	$\frac{c_p}{\text{kg}} \cdot \text{K}$
18.5	0.088	1.306	139.2
19.0	0.117	1.265	134.8
19.5	0.147	1.234	131.6

TABLE 4 : The value of different parameters in equation (19)

$m_0$ (gm)	$m_s$ (gm)	$m_h$ (gm)	$m_{mix}$ (gm)	$\frac{c_0}{\text{gm}} \cdot \text{K}$	$\frac{c_s}{\text{gm}} \cdot \text{K}$	$\frac{c_h}{\text{gm}} \cdot \text{K}$
81.2519	0.8800	15.0390	143.9011	0.75	0.45	0.84

TABLE 5 : Joule's constant of different quantities of cyclohexane-phenol

T (°C)	$\Delta T = 25 - T$ (°C)	Time (sec)	I (Amp)	V (volt)	W (J)	$\frac{c_p}{\text{kg}} \cdot \text{K}$	H (Calorie)	J (Calorie/ J)
18.5	6.5	4219	0.94	10.22	42260	139.2	135423	3.20
19.0	6.0	2978	0.94	10.22	28609	134.8	121068	4.23
19.5	5.5	2252	0.94	10.22	21635	131.6	108354	5.01

TABLE 6 : Summary of values of constants measured or calculated in this work

Constant measured or calculated	Value
$T_c$	17.0 °C
$\chi_c$	2.70% by weight of phenol
$n_{0D}$	1.4276
$\chi_n$	0.00156
$c_{pc}$	$\frac{J}{kg} \cdot K$ 106.6
J	4.15 Calorie/J

ranges are given in TABLE (5).

The average Joule's constant value is 4.15 Calorie/J. The average value for Joule's constant for cyclohexane-phenol binary mixture is less than the Joule's constant for water (4.1860 Calorie/J). This small deviation between the two values is due to the change in temperature ranges at which Joule's constants are calculated.

## CONCLUSION

The mode coupling theory of the anomalous dynamic shear viscosity near the critical point has been studied for cyclohexane - phenol binary liquid mixture.

The critical temperature  $T_c$  and critical concentration  $\chi_c$  values have been measured of cyclohexane-phenol binary mixture.

Shear viscosity coefficients and some thermodynamic properties about the binary mixtures are important for the scientists working on the improvement of molecular theories.

The behavior of refractive index of cyclohexane-phenol obeys power law universality above the phase transition. The noncritical part of refractive index has been obtained; the universal critical exponent for refractive index  $n_{0D}$  has also been calculated.

The isobaric specific heat for the critical binary mixture has been calculated using two scale factor universality. The value of Joule's constant J of cyclohexane-phenol binary mixture has been calculated.

The experimental values  $T_c, \chi_c, n_{0D}, \chi_n, c_{pc}$  and Joule's constant of cyclohexane-phenol are calculated in this work to the first time. Such values

give more characteristic properties for cyclohexane/phenol binary mixture.

The results of the different properties that have been calculated and measured of the binary liquid mixture cyclohexane-phenol are summarized in TABLE (6).

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