Two Binary Liquid Critical Mixtures Belong to Class of Universality

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Abstract

The dynamic shear viscosity of a binary liquid mixture phenol–water has been measured at different temperatures (50.0°C ≤ T ≤ 75.0°C) and different concentrations (0.00% up to 100.00% by weight of phenol). The critical temperature $T_c$ and critical concentration $x_c$ are found to be 67.0°C and 33.90% by weight of phenol respectively, the critical mass density $\rho_c$ is measured to be 0.8952 g/cm$^3$. The critical and background amplitudes of specific heat at constant pressure are calculated to be 78.12 J/kg.K and 85.29 J/kg.K respectively. The pressure derivative of the critical temperature along the critical line $\frac{\partial T}{\partial T}$ is calculated to be 9.722 ×10$^{-6}$ K/Pa.

In addition, dynamic shear viscosity of binary liquid mixture phenol–cyclohexane has been measured at different temperatures (14.0°C ≤ T ≤ 30.0°C) and different concentrations (2.00% up to 39.70% by weight of phenol). The critical temperature $T_c$ and critical concentration $x_c$ are found to be 17.0°C and 2.70% by weight of phenol respectively; the critical mass density $\rho_c$ is measured to be 0.7627 g/cm$^3$. The critical and background amplitudes of isobaric thermal expansion coefficient $\alpha_q$ and $\alpha_c$ are calculated to be 8×10$^{-5}$ K$^{-1}$ and 6×10$^{-4}$ K$^{-1}$ respectively. The pressure derivative of the critical temperature $\frac{\partial T}{\partial T}$ for the binary liquid is calculated to be 2.8572 ×10$^{-5}$ K/Pa. The universal quantity $R_+$ for the binary liquid mixture critical phenol–water is calculated to be 0.2716 ± 0.0005. In addition, the universal quantity $R_+$ for the binary liquid critical mixture phenol–cyclohexane is calculated to be 0.2699 ± 0.0001. The calculated values of the universal quantity $R_+$ are in a good agreement with the theoretical value of $R_+$, which is equal 0.2710. The two binary liquid critical mixture belong to the class of universality “Two–Scale–Factor Universality”.

Keywords: Binary liquid; Critical mixture; Homogeneous

Introduction

Binary liquid mixtures and critical point

Mixtures are the product of a mechanical blending or mixing of chemical substances like elements and compounds, without chemical bonding or other chemical changes, so that each ingredient substance retains its own chemical properties [1]. Mixtures can be either homogeneous or heterogeneous. A homogeneous mixture is a type of mixture in which the composition is uniform and every part of the solution has the same properties. A heterogeneous mixture is a type of mixture in which the components can be seen, as there are two or more phases present.

Binary liquid mixtures are combination of two pure liquid substances, which have a limited solubility of each one in the other [2]. Critical point is the point at which phase transition occurs at certain temperature called critical temperature and concentration [3]. The critical point represents the boundary between regions of homogeneous and heterogeneous behavior in phase diagrams for mixtures [4]. Hypothesis of universality greatly reduces the variety of different types of critical behavior by classifying all systems into a small number of equivalence classes [5].

The phenomenological theory of scaling has been extremely useful in understanding critical phenomena in model systems and in real materials [5]. The first characteristic of a universality class is that all the systems have the same critical exponents. In addition, the equation of state, the correlation functions and other quantities become identical near criticality, provided one matches the scales of the order parameter, the ordering field, the correlation length and the correlation time [5].

A property of hyper scaling or hyper universality (Two–Scale–Factor Universality) applies to systems in the universality classes of fluctuation-dominated (i.e., non-mean-field) critical behavior. These ideas were first developed phenomenologically and later confirmed by explicit renormalization group (RG) calculations [5]. The RG theory of critical phenomena has elucidated the mathematical mechanism for scaling and universality, and has provided a number of calculational tools for estimating universal properties [5].

Theory

Viscosity

The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress or tensile stress [6]. Viscosity is affected by different factors such as temperature, shear rate, catalyst, pressure, molecular weight concentration and storage age [7].

Mode coupling theory and shear viscosity of binary mixtures

The mode coupling theory explains the behavior of the binary mixtures at the critical temperature and concentration. The mode coupling approach of Kawasaki and Perl and Ferrell predicts a critical anomaly of the dynamic shear viscosity coefficient according to the law

$$\frac{\eta - \eta_0}{\eta} = A \ln \zeta + A \ln q_D$$

(2.1)

Where $\eta$, the noncritical part of the measured shear viscosity.

A is a constant which was calculated by D’Arrigo and given by $A \sim 0.054$ [10], and $q_D$ is Debye momentum cutoff. The dynamic shear viscosity is temperature dependent at the critical concentration which

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Received October 17, 2015; Accepted November 10, 2015; Published November 20, 2015

Citation: Ata BN, Abderaziq IR (2015) Two Binary Liquid Critical Mixtures Belong to Class of Universality. J Material Sci Eng 5: 211. doi:10.4172/2169-0022.1000211

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is given by the power law [11,12].
\[ \eta = \eta_0 t^{-\nu} \]  
(2.2)

Where \( t \) is the reduced temperature \( t = \frac{T - T_c}{T_c} \), \( \chi \) and \( \nu \) are critical exponents where \( \chi_\nu \nu = 0.04 \) [10,11].

Two–scale–factor universality

The Two–Scale–Factor Universality has been used in modern theories to explain the critical phenomena of binary liquid mixtures by predicting \( R_\xi \) [13]. The Two–Scale–Factor Universality hypothesis states that the critical amplitudes do not depend on three different scales of parameter (length, temperature, external field) but only on two scales of parameter [14]. Most of the observed quantities depend only on the dimensionless of the space (d) and of the order parameter (n) [15].

The fluid and binary mixtures transitions belong to the same class of universality d=3, n=1[16]. All binary liquid mixtures with critical mixing points belong to the same universality class. The universality concept offers the possibility to relate critical amplitudes of these systems. The exponents are universal and related by the so-called scaling laws [16].

The amplitudes of the correlation length, thermal expansion and specific heat can be deduced using the universal amplitude combinations [15,17-19]. Correlation length is a measure of the distances over which the spin–spin (or density–density) correlations in the system extend [20]. The correlation length of a binary mixture at critical composition exhibits an anomalous behavior conforming to the following exponential law:
\[ \xi = \xi_0 t^{\nu}, T > T_c \]  
(2.3)

Where \( \nu \) is a critical exponent which accepted to be 0.630 ± 0.001, \( \xi_0 \) is the critical amplitude and \( t \) is the reduced temperature \( t = \frac{T - T_c}{T_c} \) where \( T_c \) is the critical temperature [21].

The specific heat at constant pressure \( c_p \) in zero field is singular and is given by:
\[ c_p = c_{p0} + c_{p0}^\ast t^{\alpha}, T > T_c \]  
(2.4)

Where \( c_{p0} \) and \( c_{p0}^\ast \) are the critical and background amplitudes of the specific heat and \( \alpha = 0.11 \) is the critical exponent [6, 22, 23, 24].

The asymptotic behavior of the thermal expansion \( \alpha_p \) can be represented by power law of the form,
\[ \alpha_p = \alpha_p^\ast t^{\alpha_p^\ast}, T > T_c \]  
(2.5)

Where \( \alpha_p \) and \( \alpha_p^\ast \) are the critical and the background amplitudes of the thermal expansion [16]. With these three amplitudes \( \xi_0, c_{p0}^\ast \) and \( \alpha_p^\ast \) it is possible to construct a quantity, denoted \( R_\xi \), which is universal in the same sense as critical indices are universal. This quantity is defined as:
\[ R_\xi = \xi_0 \left( \frac{\hat{\alpha} c_{p0}^{\ast 1/2}}{K_s} \right)^{\nu/2} = \xi_0 \left( \frac{\hat{\alpha}^\ast T_c}{T_c} \right)^{\nu/2} \]  
(2.6)

Where \( d=3 \) is the dimension of the space, \( K_s \) is Boltzman’s constant, \( \rho_c \) is the density of the critical mixture at critical temperature \( T_c \) and concentration \( \bar{T}_c = \frac{dT_c}{d\rho} \) is the pressure derivative of the critical temperature along the critical line [16]. The theoretical value of the universal constant \( R_\xi = \nu \left( \frac{\pi}{4g} \right)^{\nu/2} \) in three dimensions for \( n = 1, d = 3 \) and \( \nu = 0.64 \) which equal 0.2710 [16].

Experimental

Methodology

In this work two binary mixtures were used the phenol–water binary mixture and phenol–cyclohexane binary mixture. The viscosities were measured for both at different temperatures and concentrations. The critical temperature, concentration, heat capacity at constant pressure and density were measured of each mixture.

Experimental Apparatus

Viscosity Apparatus:

- **Capillary Viscometer:** is a device used to measure the viscosity of the liquid with a known density by measuring the time for a known volume of the liquid to flow through the capillary under the influence of gravity [25].
- **Brookfield Digital Viscometer Model DV-1+:** It measures the viscosity of a liquid in centipoises with accuracy ± 1%. It is used to measure the dynamic viscosity from 1 up to 103 x 106, cP.

Density Apparatus: A pycnometer is used to measure the density of the mixtures and pure substances. The Analytical Balance HR-200: It is used to measure the mass in gm unit with accuracy of ± 0.00005%.

Temperature Apparatus: Digital Primia long Thermometer is used to measure the temperature of the samples with accuracy ± 1%, the range of the temperature from -20 up to 100°C. Julabo F25-MV Refrigerated and Heating Circulator is used to control the temperature of the samples with accuracy 1%.

The calorimeter: It is an instrument used to measure the heat of chemical reactions or physical changes as well as heat capacity. A calorimeter has been constructed with glass pyrex beaker instead of the aluminum, and a nichrome resistance wire covered by a U–tube glass. This calorimeter has been constructed to avoid the reaction of phenol with metals.

Results and Discussion

Viscosity measurements

Phenol–Water Binary Mixture: The results of the dynamic viscosity \( \eta \) as a function of temperature for different concentrations of phenol–water binary mixture are evaluated. The dynamic shear viscosities of phenol–water binary mixture are plotted as a function of temperature at different concentrations of phenol in appendix B. The critical temperature occurs when the two phases of the binary mixture become one phase which appears as anomaly at 67.0°C for the concentration 33.90% by weight of phenol, as shown in Figure 1. In addition, the mixture was visually observed as one phase at the critical temperature and concentration.

Phenol–cyclohexane binary mixture: The results of the dynamic viscosity \( \eta \) as a function of temperature for different concentrations of phenol–cyclohexane binary mixture are evaluated. The dynamic shear viscosities of phenol–cyclohexane binary mixture are plotted as a function of temperature at different concentrations of phenol in appendix B.
mixture become one phase which appears as anomaly at 17.0°C for the concentration 2.70% by weight of phenol, as shown in Figure 2. In addition, the mixture was visually observed as one phase at the critical temperature and concentration.

Mass density measurements

**Phenol–Water Binary Mixture:** The critical mass density \( \rho_c = 0.8952 \text{ g/cm}^3 \pm 0.0001 \) at the critical concentration \( x_c = 33.90\% \) by weight of phenol and the critical temperature \( T_c = 67.0^\circ \text{C} \) for the binary mixture phenol–water.

**Phenol–Cyclohexane Binary Mixture:** The critical mass density \( \rho_c = 0.7627 \text{ g/cm}^3 \pm 0.0001 \) at the critical concentration \( x_c = 2.70\% \) by weight of phenol and the critical temperature \( T_c = 17.0^\circ \text{C} \) for the binary mixture phenol–cyclohexane.

Specific heat measurements

**Phenol–water binary mixture:** The specific heat at constant pressure \( c_p \) for the binary mixture phenol–water is calculated using the relation:

\[
W = IVt = (m_c c_p + m_b c_p) \Delta T
\]

The specific heat at constant pressure is given by relation (2.4) which is

\[
c_p = c_p^c \tau^{-\alpha} + c_p^b
\]

Where \( t \) is the reduced temperature and \( \alpha \) is the critical exponent which equals 0.11. The specific heat at constant pressure and \( \tau^* \) at different temperatures are presented in Table 1.

The specific heat at constant pressure is plotted with \( \tau^* \) in Figure 3, using the relation

\[
c_p = c_p^c \tau^{-\alpha} + c_p^b
\]

The slope of the line is \( c_p^c = 78.12 \pm 0.04 \text{ J/kg.K} \), which is the critical amplitude of specific heat at constant pressure of the binary mixture phenol–water, and the intercept is \( c_p^b = 85.29 \pm 0.02 \text{ J/kg.K} \) which is the background amplitude of specific heat at constant pressure.

Calculation of the universal quantity \( R^* \)

The Two–Scale–Factor Universality relation (2.6),

\[
R^* = \left( \frac{\alpha T_c}{K_B} \right)^{1/d} \tau^{-\alpha + \alpha} \rho_c
\]

The universal quantity \( R^* \) can be calculated using the first term

\[
R^*_1 = \left( \frac{\alpha T_c}{K_B} \right)^{1/d} \rho_c
\]

Where the critical exponent \( \alpha = 0.11 \), Boltzmann’s constant \( K_B = 1.38 \times 10^{-23} \text{ J/K} \), and the dimensionality \( d = 3 \).

**Phenol–water binary mixture:** The universal quantity \( R^*_c \) can be calculated for the binary mixture phenol–water to be 0.2716 \( \pm 0.0125 \) by substituting the values of \( c_p^c = 78.12 \text{ J/kg.K} \), \( \rho_c = 0.8952 \text{ gm/cm}^3 \),

| Temperature (°C) | \( T - T_c \) | \( \tau^* \) | \( c_p^b \) (J/kg.K) |
|------------------|---------------|-------------|---------------------|
| 68.0             | 0.014925      | 1.588065    | 30.4                |
| 68.5             | 0.022388      | 1.518792    | 29.9                |
| 69.0             | 0.026981      | 1.471482    | 29.4                |
| 69.5             | 0.037313      | 1.435803    | 28.6                |
| 70.0             | 0.044776      | 1.407294    | 27.2                |
| 71.0             | 0.059701      | 1.363458    | 23.5                |
| 72.0             | 0.074627      | 1.330398    | 19.5                |
| 73.0             | 0.089552      | 1.303982    | 16.4                |
| 74.0             | 0.104478      | 1.282057    | 13.7                |
| 75.0             | 0.119403      | 1.263364    | 10.9                |

Table 1: Specific heat data of binary mixture phenol-water.

**Figure 3:** The specific heat at constant pressure \( c_p \) versus \( \tau^* \) for binary mixture phenol–water.
and ξ = 3.3Å [26]. The theoretical value of \( R_0 = \sqrt{\frac{n}{2\pi} R_0} \) in three dimensions for \( n = 1, d = 3 \) and \( v = 0.64 \), equal 0.2710.

**Phenol–cyclohexane binary mixture:** The universal quantity \( R_0^{+} \), can be calculated for the binary mixture phenol–cyclohexane to be \( 0.2699 \pm 0.0125 \) by substituting the values of \( \xi = 106.60 \text{J/kg.K} \) [27], \( \rho_c = 0.7627 \text{gm/cm}^3 \), and \( \xi = 3.12 \text{Å} \). The theoretical value of \( R_0^{+} = 0.2710 \). This indicates that the two binary liquid critical mixtures phenol–water and phenol–cyclohexane belong to the same class of universality “Two–Scale–Factor Universality”.

**Calculation of \( T_0^{+} \)**

The Two–Scale–Factor Universality relation (2.6),

\[
R_0^{+} = \xi \left( \frac{\alpha_{p\rho}}{K_p} \right)^{\frac{1}{d}} = \xi \left( \frac{\alpha_{pc} \rho}{K_p} \right)^{\frac{1}{d}}
\]

(2.6)

The pressure derivative of the critical temperature along the critical line \( T_0^{+} \), can be calculated using the second term

\[
R_0^{+} = \xi \left( \frac{\alpha_{pc} \rho}{K_p} \right)^{\frac{1}{d}}
\]

**Phenol–water binary mixture:** The pressure derivative of the critical temperature along the critical line \( T_0^{+} \) for the binary mixture phenol–water can be calculated to be \( 9.722 \times 10^{-6} \text{K/Pa} \). The values of \( T_0^{+} = 340 \text{K} \), \( \alpha_{pc} = 0.002 \text{K}^{-1} \) [26], \( \xi = 3.3 \text{Å} \) [26] and \( R_0^{+} = 0.2716 \).

**Phenol–cyclohexene binary mixture**

The critical amplitude of isobaric thermal expansion coefficient \( \alpha_{pc} \) is need to calculate \( T_0^{+} \). The isobaric thermal expansion coefficient \( \alpha_{pc} \) can be calculated using the relation:

\[
\alpha_{pc} = \frac{1}{V} \left( \frac{dT}{dP} \right)_{\text{isobaric}}
\]

(4.1)

Where, \( V \) is the volume, \( T \) is the temperature and \( P \) is the pressure. Equation 4.1 could be expressed in another form by applying \( V = \frac{m}{\rho} \).

\[
\alpha_{pc} = -\frac{1}{\rho} \left( \frac{d\rho}{dT} \right)_{\text{isobaric}} = \alpha_p = \rho \left( \frac{d\rho^{-1}}{dT} \right)
\]

(4.2)

Where, \( m \) is the mass and \( \rho \) is the density of the binary mixture. The values of the density and its reciprocal at different temperatures above the critical point are presented in Table 2. The reciprocal of the density is fitted with the corresponding temperatures and the slope \( \left( \frac{d\rho^{-1}}{dT} \right) \) is determined from Figure 4.

**Table 2:** The mass density and its reciprocal values at different temperatures for the binary mixture phenol - cyclohexane.

| T(K) | Mass density \( \rho \)(gm/cm\(^3\)) | \( \rho^{-1} \)(gm/cm\(^3\)) |
|------|---------------------------------|---------------------|
| 290.5 | 0.7376                           | 1.3561 |
| 291.0 | 0.7374                           | 1.3565 |
| 291.5 | 0.7372                           | 1.3568 |
| 292.0 | 0.7370                           | 1.3572 |
| 292.5 | 0.7368                           | 1.3574 |
| 293.0 | 0.7376                           | 1.3579 |
| 293.5 | 0.7364                           | 1.3589 |
| 294.0 | 0.7359                           | 1.3592 |
| 295.0 | 0.7357                           | 1.3602 |
| 298.0 | 0.7352                           | 1.3616 |

The slope from Figure 5 is \( \frac{d\rho^{-1}}{dT} = 0.0008 \text{ cm}^3/\text{g. K} \).

The critical and the background isobaric thermal expansion coefficients can be determined by linear fitting of the isobaric thermal expansion coefficient \( \alpha_p \) versus \( \tau \), where \( \tau = \frac{T - T_c}{\xi} \) and \( \alpha = 0.11 \) depending on the relation:

\[
\alpha_p = \alpha_p^{\text{critical}} + \alpha_p^{\text{background}}
\]

(2.4)

The values of \( \alpha_p \) are calculated using equation (4.2) and the data are presented in Table 3. The data of the isobaric thermal expansion coefficient \( \alpha_p \) are plotted versus \( \tau^{-0.11} \) as shown in Figure 5. The slope of the line represents the critical isobaric thermal expansion coefficient \( \alpha_p^{\text{critical}} = 8 \times 10^{-6} \text{K}^{-1} \), and the intercept of the line represents the background isobaric thermal expansion coefficient \( \alpha_p^{\text{background}} = 6 \times 10^{-4} \text{K}^{-1} \).

The pressure derivative of the critical temperature along the critical line \( T_0^{+} \) for the binary mixture phenol–cyclohexene is calculated to be \( 78.11 \text{K} \) and \( 85.29 \text{J/kg.K} \) respectively.

**Conclusion**

The dynamic shear viscosity of two binary liquid mixtures phenol–water and phenol–cyclohexene has been measured at different temperatures and concentrations. The critical temperature and critical concentration for the binary liquid mixture phenol–water were \( T_c = 67.0^\circ \text{C} \) and \( x_c = 33.90 \) by weight of phenol. The critical density \( \rho_c \) for the binary liquid mixture phenol–water was found to be 0.8952 g/cm\(^3\) at the critical temperature and concentration.

The specific heat at constant pressure \( cp \) of the binary liquid mixture phenol–water has been measured; the critical \( cp \) and back ground \( cpb \) amplitudes of the specific heat at constant pressure have been calculated to be 78.11 J/kg.K and 85.29 J/kg.K respectively.
The isobaric thermal expansion coefficient $\alpha$ at different temperatures, the isobaric thermal expansion coefficient $\alpha$ for phenol–cyclohexane mixture are calculated at different temperatures, the isobaric thermal expansion coefficient $\alpha$ for phenol–water mixture is determined to be $9.722 \times 10^{-6} \text{K/Pa}$. The isobaric thermal expansion coefficient $\alpha$ for phenol–cyclohexane mixture is calculated to be $2.8572 \times 10^{-8} \text{K/Pa}$. The isobaric thermal expansion coefficient $\alpha$ for phenol–water mixture is determined to be $8 \times 10^{-6} \text{K}^{-1}, 6 \times 10^{-4} \text{K}^{-1}$ respectively. The measured and calculated parameters for phenol–cyclohexane binary mixture are summarized in Table 5. The universal quantity $R + \xi$ is calculated from field theory. Physical Review B 21: 5427.

The pressure derivative of the critical temperature along the critical line $T'_c$ is calculated for the binary mixture phenol–water to $69.0^\circ \text{C}$ (b) $34.0\%$ (b) $24.0\%$ (b) $298.0$ $1.484307$ $0.7627 \text{g/cm}^3$ $33.90\%$ $0.000588$ $8 \times 10^{-4} \text{K}^{-1}$ $6 \times 10^{-4} \text{K}^{-1}$ $0.000589$ $78.11$ $85.292$ $9.722 \times 10^{-6} \text{K/Pa}$ $0.2716$ $292.0$ $0.000589$ $1.728823$ $292.5$ $0.000589$ $1.866904$ $293.0$ $0.000589$ $1.65341$ $293.5$ $0.000589$ $1.62561$ $294.0$ $0.000589$ $1.601907$ $293.0$ $0.000589$ $1.65341$ $293.0$ $0.000589$ $1.65341$ $293.5$ $0.000589$ $1.62561$ $294.0$ $0.000589$ $1.601907$ $295.0$ $0.000588$ $1.563065$ $298.0$ $0.000588$ $1.484307$
25. Generalic E (2014) Glass capillary viscometer. Croatin-English Chemistry Dictionary and Glossary.

26. Abdelraziq IR (2015) Unpublished work.

27. Hussein GF, Ashqer I, Saadeddin I (2015) Critical behavior of the density of binary liquid mixture cyclohexane–phenol. An-Najah National University.

28. Reehan M, Ashqer I, Abu-Jafar M (2015) Critical behavior of the ultrasonic attenuation for the binary mixture of water and phenol. An-Najah National University.

29. Howell OR (1932) A study of the system water-phenol: I densities. Proceedings of the Royal Society of London A 137: 418-433.

30. Krishnan RS (1935) Molecular clustering in binary liquid mixtures. Proceedings of the Indian Academy of Science 1: 915-927.