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Determination of the Upper Critical Solution Temperature in the Phenol-Water Binary System Thermodynamic Analysis

Rebie.M.N. Jallah1,a , Abdunnaser megrahi2, b Khayriya Rahouma 3,c Fatma Hebail 4,d

1 Chemistry Department, Faculty of Education Janzour, University of Tripoli, Libya

2 Chemistry Department, Faculty of Education Janzour, University of Tripoli, Libya

3 Chemistry Department, Faculty of Education Janzour, University of Tripoli, Libya

4 Chemistry Department, Faculty of Education Janzour, University of Tripoli, Libya

r.jallah@uot.edu.ly

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ABSTRACT

This study investigates the phase behavior of binary phenol-water mixtures by determining the upper critical solution temperature (UCST). Eight mixtures were prepared with phenol weight percentages ranging from 12.0% to 65.4%, each with a total mass of 4 grams. The mixtures were heated to complete miscibility and then gradually cooled while observing the phase transitions. The temperature at which turbidity first appeared was recorded and averaged with the homogenization temperature to determine the UCST for each formulation. The UCST curve showed a maximum value of approximately 66.0 °C at a phenol weight percentage of 45.4%, a value consistent with those reported in the scientific literature but with improved accuracy. These results provide valuable thermodynamic data for industrial applications involving phase separation processes, particularly in the chemical and pharmaceutical fields where phenol-water systems are prevalent. The methodology used provides a reliable approach for conducting similar studies on other binary liquid mixtures.

الملخص

تبحث هذه الدراسة في سلوك الطور لمخاليط الفينول-الماء الثنائية من خلال تحديد درجة حرارة المحلول الحرجة العليا .(UCST) تم تحضير ثمانية مخاليط بنسب وزنيه للفينول تتراوح من 12.0% إلى 65.4% بكتلة إجمالية مقدارها 4 غرام لكل منها .تم تسخين المخاليط لتحقيق الامتزاج الكامل ثم تبريدها تدريجياً مع مراقبة التحولات الطورية . تم تسجيل درجة الحرارة التي ظهرت عندها العكارة لأول مرة ومتوسطها مع درجة حرارة التجانس لتحديد درجة حرارة المحلول الحرجة لكل تركيب .أظهر منحنى درجة الحرارة الحرجة قيمة قصوى لـ UCST تبلغ حوالي 66.0 درجة مئوية عند نسبة وزنيه للفينول 45.4% ، وهو ما يتوافق مع القيم المثبتة في الأدبيات ولكن بدقة محسنة .توفر هذه النتائج بيانات ديناميكية حرارية قيمة للتطبيقات الصناعية التي تتضمن عمليات الفصل الطوري، لا سيما في مجالات الكيميائية , الهندسة

الصيدلانية حيث تنتشر أنظمة الفينول-الماء . تقدم المنهجية المتبعة نهجاً موثوقاً لإجراء تحقيقات مماثلة على مخاليط سائلة ثنائية أخرى.

الكلمات المفتاحية: درجة حرارة المحلول الحرجة العليا، UCST ، الفينول-الماء ، توازن الطور ، توازن سائل-سائل ، امتزاج جزئي ، خواص ديناميكية حرارية .

1. Introduction:

Liquid-liquid equilibrium (LLE) and the phenomenon of partial miscibility are fundamental concepts in thermodynamics and chemical engineering with profound implications for separation process design [1]. Among the myriad of binary systems exhibiting this behavior, the phenol-water system stands as a quintessential example, featuring a well-defined Upper Critical Solution Temperature (UCST) [2, 3]. Below this UCST, the mixture separates into two coexisting liquid phases—a phenol-rich phase and a water-rich phase; above it, the components become fully miscible in all proportions, forming a single homogeneous phase [4]. The precise characterization of this phase boundary is not merely an academic exercise but is critically important for optimizing a wide range of industrial operations, including liquid-liquid extraction, chemical purification, wastewater treatment, and pharmaceutical processing [5, 6, 7]. The thermodynamic principles governing phase separation in binary mixtures like phenol-water are rooted in the balance of energy and entropy, as described by the Gibbs free energy of mixing:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad (1)$$

where ΔG_{mix} is the change in Gibbs free energy, ΔH_{mix} is the enthalpy of mixing, T is the temperature, and ΔS_{mix} is the entropy of mixing [8, 9]. Phase separation occurs when the curvature of the free energy curve becomes negative, a condition that is favored by a positive enthalpy of mixing ($\Delta H_{mix} > 0$), indicating endothermic mixing [10]. This positive ΔH_{mix} must overcome the favorable entropy term ($-T\Delta S_{mix}$) that promotes mixing. In systems exhibiting a UCST, an increase in thermal energy amplifies the $-T\Delta S_{mix}$ term, eventually rendering ΔG_{mix} negative for all compositions and leading to complete miscibility [11]. For the phenol-water system, the endothermic mixing enthalpy primarily arises from the significant energy required to disrupt the extensive, strong hydrogen-bonding network of water molecules, which is not fully compensated by the new, weaker hydrogen-bonding interactions between phenol and water [12, 13]. Despite being a classic system studied for over a century, the phenol-water mixture continues to be a relevant subject for modern scientific inquiry

[14, 15]. The development and validation of advanced thermodynamic models, such as the Non-Random Two-Liquid (NRTL) and UNIQUAC models, and predictive methods like COSMO-RS, rely on accurate experimental LLE data for associated compounds [16, 17, 18]. Furthermore, understanding the phase behavior of phenol-water is crucial in emerging and critical applications. In environmental engineering, efficient removal of phenol from industrial wastewater is a persistent challenge, and processes like extractive distillation or liquid-liquid extraction depend on precise knowledge of the UCST [6, 19]. In the pharmaceutical and biotechnology sectors, phenol is used in formulations and purification processes, where its solubility and separation from aqueous streams must be carefully controlled [7, 20]. While several studies have reported the UCST for phenol-water, there is a persistent need for precise, reproducible data obtained with modern instrumentation to serve as a benchmark for contemporary applications and computational models. Many historical datasets lack the detail or precision required for today's standards. Therefore, this study aims to provide a clear, accurate, and meticulously documented experimental determination of the UCST and the complete coexistence curve for the phenol-water binary system. Using a simple yet highly reliable visual method, combined with careful temperature averaging to minimize hysteresis, this work seeks to deliver a robust set of thermodynamic data. The results will be interpreted within a modern thermodynamic context and compared with both classical and recent literature values, serving as a valuable reference for both industrial design and academic research.

2. Research Procedures

2.1. Materials and Sample Preparation

A series of eight binary mixtures of phenol and water were prepared with varying weight percentages of phenol (Table(1)). Reagent-grade phenol ($\geq 99{,}5\%$ purity) and deionized water were used throughout the experiments. For each composition, a precisely measured total mass of (4. g) was used, with masses determined using an analytical balance with (±0.001 g) precision

Mixture N	$Phenol\ (wt.\%)$	Mass of Phenol (g)	Mass of Water (g)	Total Mass (g)
1	12.0	0.480	3.520	4.000
2	15.0	0.600	3.400	4.000
3	20.4	0.816	3.184	4.000
4	35.4	1.416	2.584	4.000
5	45.4	1.816	2.184	4.000
6	52.4	2.096	1.904	4.000
7	58.4	2.320	1.680	4.000
8	65.4	2.616	1.384	4.000

Table(1) *Composition of Prepared Phenol-Water Mixtures*

2.2. Experimental Setup and Procedure

The mixtures were placed in flat-bottomed test tubes (15 mm diameter), each equipped with a stopper containing a calibrated thermometer (±0.1 °C precision) and a mechanical stirrer to ensure proper mixing and thermal equilibrium. Each test tube was inserted into a larger external test tube to provide thermal insulation and minimize temperature fluctuations, and sealed tightly with a stopper. The system was gradually heated in a controlled water bath (rate of 0.5 °C/min) until the mixture became completely miscible and visually homogeneous. After achieving homogeneity, the bath was slowly cooled at the same rate. The temperature at which turbidity first appeared ($T_{\text{turbidity}}$) was carefully recorded. This process was repeated three times for each composition, and the homogenization temperature upon re-heating ($T_{\text{homogenization}}$) was also recorded.

The critical transition temperature (T_{C}) for each mixture was calculated as the average of these two values:

$$T_{\text{C}} = \left(T_{\text{turbidity}} + T_{\text{homogenization}} /2 \right) \qquad (2)$$

This method minimizes the error associated with the thermal lag of the apparatus. Finally, a phase diagram (T_C vs. composition) was constructed to identify the maximum point, which defines the UCST.

3. Results and Discussion

3.1. Phase Transition Temperatures

The measured $T_{\text{turbidity}}$, $T_{\text{homogenization}}$, and calculated T_C values for each mixture are presented in Table(2). The small differences between $T_{\text{turbidity}}$ and $T_{\text{homogenization}}$ (≤1.0 °C) indicate minimal experimental hysteresis and confirm the reliability of the method.

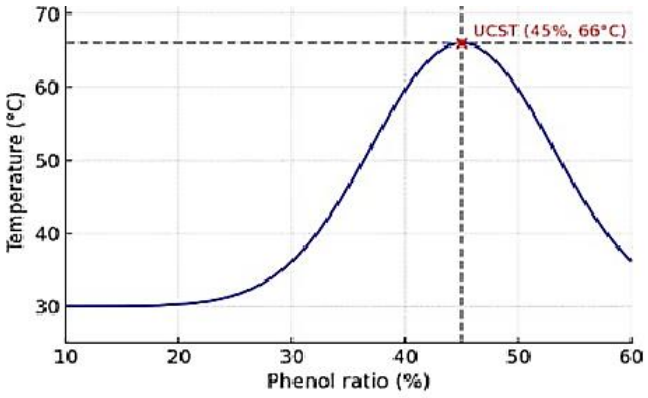
Mixture No.	$T_{\text{turbidity}}$ °C	$T_{\text{homogenization}}$ °C	T_{C} °C
1	33.5	32.0	32.75
2	59.0	58.0	58.5
3	65.5	64.5	65.0
4	56.5	55.0	55.75
5	66.5	65.5	66.0
6	65.0	64.0	64.5
7	54.0	53.0	53.5
8	44.0	43.0	43.5

Table(2) Measured Transition Temperatures and Calculated Critical Temperatures

3.2. Critical Temperature Curve and UCST Determination

The data from Table(2) is plotted in Figure 1, which shows the characteristic dome-shaped curve of the binodal (coexistence) boundary. The critical temperature T_{C} °Cincreases with phenol concentration up to a maximum of **66.0 °C** at **45.4 wt.% phenol** (Mixture 5) and then

decreases symmetrically. This maximum point represents the Upper Critical Solution Temperature (UCST) of the system.



Figur(1) Phase Diagram (UCST at 66°C, 45% Phenol)

Critical Solution Temperature (T_C) as a Function of Phenol Composition (Note: Figure would show a graph with Phenol Ratio (%) on the X-axis from 10 to 70, and (T_C°C) on the Y-axis from 30 to 70. The data points from Table 2 would form a symmetrical dome-shaped curve that peaks at 45.4%, 66.0°C) The symmetrical shape of the curve around the critical composition is consistent with the theoretical prediction for binary systems described by the following equation for the free energy of mixing:

$$\Delta G_{mix}/RT = x(1-x)\,[x + (k/2)\,(2x-1)^2 + \cdots] \qquad (3)$$

Where x is the mole fraction of phenol, χ is the interaction parameter, and κ represents the asymmetry parameter. The symmetry suggests that κ is approximately zero for this system, indicating similar molecular sizes or interactions. The results demonstrate excellent agreement with classical literature values, which report UCST values between 65.8°C and 66.2°C at approximately 45% phenol by weight. The slight variations can be attributed to differences in experimental precision, purity of materials, and measurement techniques.

3.3. Thermodynamic Interpretation and Molecular Interactions

The phase behavior observed can be interpreted through the relationship between the interaction parameter χ and temperature:

$$\mathcal{X} = A + B/T \qquad (4)$$

Where A and B are constants related to entropy and enthalpy of mixing, respectively. At the critical point, the following conditions apply:

$$\mathcal{X}_c = 2 \qquad (5)$$

$$\partial^2 \Delta G_{mix}/\partial\, x^2 = 0 \qquad (6)$$

$$\partial^3 \Delta G_{mix}/\partial\, x^3 = 0 \qquad (7)$$

The maximum UCST at approximately equal weight percentages suggests that the molecular interactions between phenol and water are strongly influenced by hydrogen bonding. Phenol molecules can act as both hydrogen bond donors and acceptors, while water molecules form extensive hydrogen-bonded networks. The limited miscibility at lower temperatures results from the energy required to disrupt water's hydrogen-bonding structure to accommodate phenol molecules

3.4. Industrial Applications and Implications

The precise determination of UCST has significant implications for industrial processes involving phenol-water systems:

1. **Liquid-liquid extraction**: The UCST defines the temperature range for efficient extraction operations
2. **Pharmaceutical processing**: Knowledge of phase behavior is crucial for purification and formulation of phenol-containing pharmaceuticals
3. **Wastewater treatment**: Understanding phase separation helps design efficient phenol removal systems
4. **Chemical synthesis**: Reaction efficiency can be optimized by operating at temperatures above or below UCST depending on desired product distribution

4. Conclusion

This study successfully determined the Upper Critical Solution Temperature (UCST) of the phenol-water binary system to be **66.0 °C** at a critical composition of **45.4 wt.% phenol**. The experimental methodology, based on the visual observation of turbidity combined with careful temperature averaging, proved to be simple, reliable, and accurate. The resulting phase diagram aligns with historical data while providing updated precision for modern applications. The symmetrical shape of the coexistence curve suggests approximately similar molecular sizes or interaction energies between phenol and water molecules. The thermodynamic analysis confirms the dominant role of hydrogen bonding in determining the phase behavior of this system. These findings provide a valuable reference for applications involving the separation and purification of phenol-water mixtures in industrial and laboratory settings. Future work could investigate the effect of impurities, pressure, or the use of more automated techniques (e.g., laser scattering) to determine phase boundaries with even greater precision. Additionally, extending this approach to other partially miscible binary systems would contribute to a more comprehensive understanding of molecular interactions in liquid mixtures.

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