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Solubility Critical Effects in Binary Liquid Mixture

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Introduction

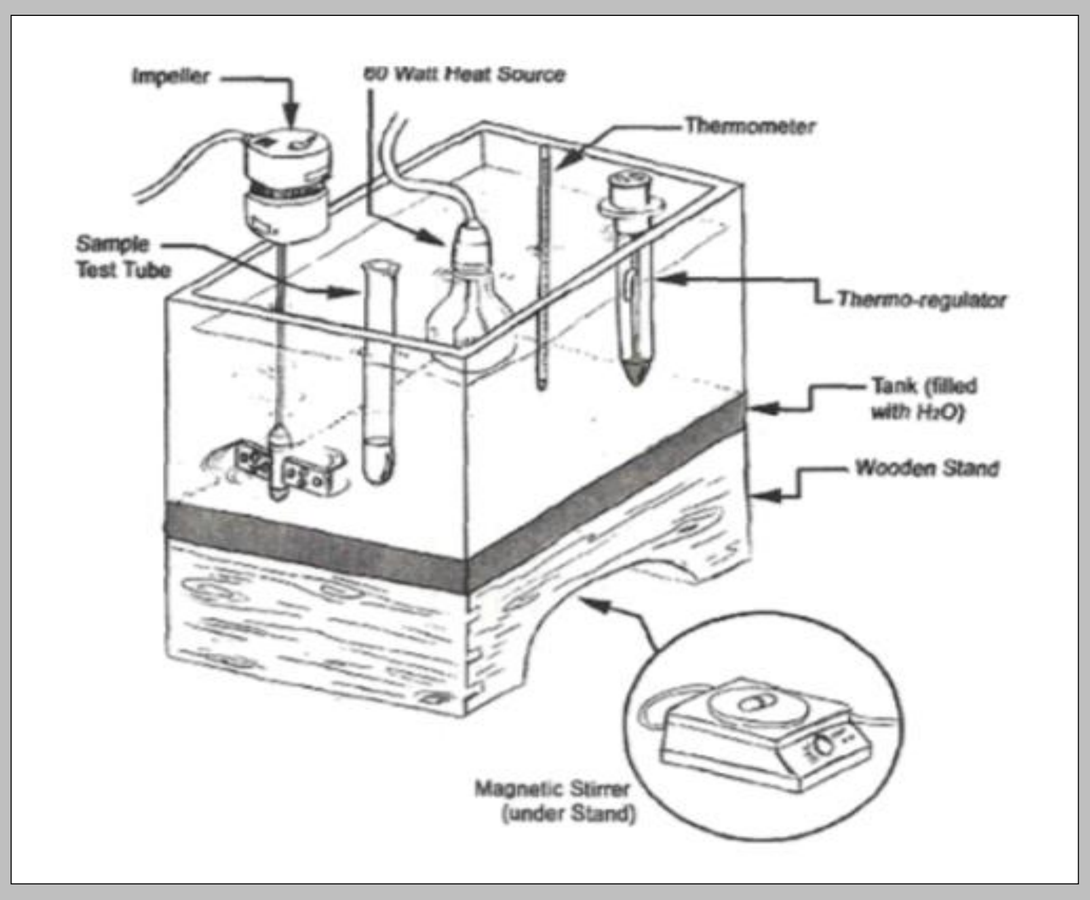
- Over 1000 pairs of liquids are known to exhibit partial miscibility over a range of compositions. The width of this range, known as the miscibility gap, is determined by the critical temperature of a solution
- Isobutyric acid (IBA) + water is a common liquid pair that exhibits a miscibility gap
- When a mixture of IBA and water is cooled through the single-phase region above its critical temperature, its heat capacity is found to diverge toward positive infinity as it nears the critical temperature
- The Principle of Critical Point Universality predicts that the heat capacity is the temperature rate of change of chemical solubility involving a solid in a binary liquid mixture
- Our experiment focuses on determining the temperature dependence of the solubility of gallium oxide (Ga_2O_3)

Results

- The results of the spectroscopic analysis are expected to be available by the end of September
- If we let *s* be the solubility and *T* be the Kelvin temperature, thermodynamic theory indicates that a plot of ln *s* vs. 1/*T* should form a straight line with negative slope if Ga_2O_3 dissolves endothermically and should form a straight line with positive slope if Ga_2O_3 dissolves exothermically. The Principle of Critical Point Universality supports this trend, with values decreasing and increasing towards negative infinity and positive infinity, respectively

Methods and Materials

- A mixture of IBA + water was prepared at its critical composition of 38.8 wt.% IBA and introduced into a reaction vessel
- Solid Ga_2O_3 was added to the vessel along with a magnetic stirring bar. The vessel was then immersed in a thermoregulated water bath.
- Starting at a temperature near the critical region at 26°C, the contents of the vessel were stirred for 24 hours to achieve chemical equilibrium and then left to stand idle for an additional 24 hours
- An aliquot from the binary mixture was then transferred to a vial with 10% nitric acid. The temperature of the water bath was then raised by 1°C. This process was repeated until 16 samples were collected and analyzed via spectroscopy.



Impact and Future Research

If the results show that the Principle of Critical Point Universality applies to chemical solubility, the critical solubility effect can be applied for useful purposes. One possible application of the effect is the capture and sequestration of atmospheric carbon dioxide. The carbon dioxide can be dissolved in a critical mixture, such as triethylamine + water. Dissolution can be performed at a temperature in the critical region where the solubility is high. The mixture can then be transferred to a desorber where it is released for sequestration at a temperature where the solubility is low. In the critical region, these two temperatures will be close together, meaning minimal energy is expended to heat the mixture to release the carbon dioxide, and that minimal heat needs to be removed to return the mixture to its undersaturated absorbing state.

References

1. James K. Baird, Joshua R. Lang, Xingjian Wang, Anusree Mukherjee, and Pauline Norris. “Phase Rule and the Universality of Critical Phenomena in Chemically Reacting Liquid Mixtures.” *The Journal of Physical Chemistry B* (2019) *123* (26), 5545-5554

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