

50 years of the Institute of High Pressure Physics Polish Academy of Sciences 'RoadMaP' X-PressMatter Lab: Soft Matter, Food & Glasses under Pressure Anniversary Symposium "Unipress 50"

## Critical liquids under pressure: from fundamentals to innovative extraction technologies solutions

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**Enhanced visual method** 

The Physics of Critical Phenomena is the grand universalistic success of the last half-century of physics. It enabled the explanation of common patterns appearing, for systems different at the microscopic level, on approaching the critical temperature. It originates from Cagnard de La Tour's (1823) observation of the critical opalescence, which is still the phenomenon's hallmark. It occurs both for the gas-liquid critical point (GLCP) and critical consolute point (CCP) in binary mixtures. X-PressMatter Lab developed the innovative semi-automatic setup for determining coexistence curves even for the most challenging case of the critical point in multicomponent mixtures. Just in a few days, instead of several months using the analysis of the fractional meniscus heights. For GLCP and CCP just a few minutes are needed to determine critical parameters.

## From observation to critical parameters





Analysis of relative volumes occupied by coexisting phases allows for quick and precise calculation of critical concentrations and critical temperature – parameters of vital importance to extraction technology.

## **Critical impact on extraction**

Fluid-based extractions are one of the most significant industrial technologies and they struggle with different problems:

- Supercritical Fluid (SCF) extraction explores unique properties in the gas phase, above the gas-liquid critical point it is the most selective, but has limited efficiency, particularly for larger amounts (food, chemicals, cosmetics).
- Liquid (L) extraction, related to the dissolution of a selected component in a liquid solvent, is poorly selective and often uses toxic component thus introducing pollution (from food to chemical industry).
- Liquid-liquid (L-L) extraction, based on different solubility of processed material in two immiscible, but coexisting liquid phases separated by a meniscus, has limited efficiency, uses often toxic ingredients and generates huge amount of pollution

Above are photographs of the opalescence - which is not only milky, but has a bluish tint, captured using this setup with clearly visible movement of the menisci with temperature changes. Also above is the solution of the Cailletet-Mathias (CM) rectilinear diameter failure problem. Our method has the ability to determine phase equilibria in a challenging case of lower critical point and presents the first-ever evidence for the diameter anomaly - violating CM - for such a system.

## References

- J. Kalabiński, A. Drozd-Rzoska, S. J. Rzoska, New insight into 3-picoline deuterium oxide (D<sub>2</sub>O) mixtures of limited miscibility with the lower critical consolute temperaturę. Europ. Phys. J E topical issue on Soft Matter & Food (2022): https://arxiv.org/ftp/arxiv/papers/2207/2207.01670.pdf
- 2. A. Drozd-Rzoska, S. J. Rzoska, *Criticality-related fundamental bases for new*

(hydrometallurgy, chemical industry).

X-PressMatter works indicate new, more effective solutions, in each case exploring efficiency and selectivity boosted by the Critical Phenomena, also for (L), (L-L) technologies – where it was not considered so far.





Instead of using the classic gas domain for SCF technology (with only 5% pre-transitional anomaly strength), via the critical distortion of dielectric constant - one can shift to the sub-critical domain. Operating on the coexistence curve diameter shows a 8x boost to anomaly strength. Supplemental usage of ultrasounds provides access to the diameter as shown by red stars in the figure to the left. This is Sub-Crit technology.

For the L-L technology, using the mixture of limited miscibility (here nitrobenzene-dodecane under pressure), one can boost the anomaly strength up to 10%, reaching the criticality-related selectivity – not available for L-L technology in present applications. This is L-L-Crit technology.

- generations of gas-liquid, liquid-liquid, and liquid (L E) extraction technologies. **Europ. Phys. J E topical issue on Soft Matter & Food (2022)**: https://arxiv.org/abs/2207.01668
- 3. A. Drozd-Rzoska, S.J. Rzoska, J. Kalabiński, *The impact of pressure on low molecular weight near-critical mixtures of limited miscibility*. **ACS Omega 5**, 20141-20152 (2020)
- 4. A. Drozd-Rzoska and S.J. Rzoska, *The super- and sub- critical effects for dielectric constant in diethyl ether*. J. Chem. Phys. 144, 24506 (2016).

In X-Press Matter the extraordinary 'doubled' long-range supercriticality (related to pressure and temperature) has been discovered. This opens the gate for criticality-supported, selective Liquid extraction technology (L-Crit), with the strength of the anomaly boosted up to 16%. The question arises, if unique pro-health properties of linseed oil are not supported by 'criticality', what opens new opportunities for both research and application.

