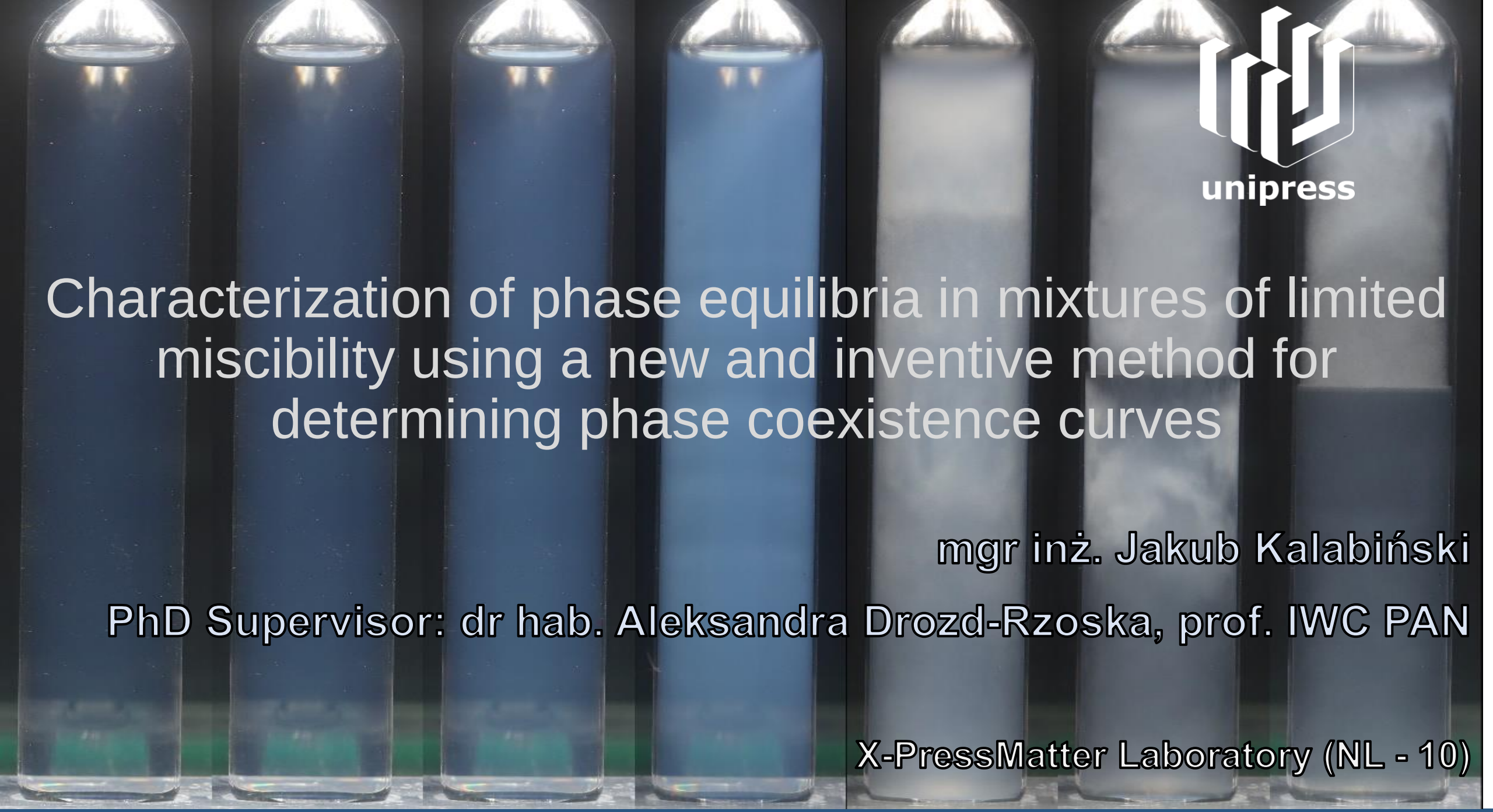

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Characterization of phase equilibria in mixtures of limited miscibility using a new and inventive method for determining phase coexistence curves

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List of publications on which the dissertation is based

1. S. J. Rzoska, J. Kalabiński, A. Drozd-Rzoska, *Critical concentration in binary mixtures of limited miscibility*. Fluid Phase Equilibria (2021).
   IF = 2.58, pkt MEiN = 100
2. J. Kalabiński, A. Drozd-Rzoska, S. J. Rzoska, *New insight into 3-picoline—deuterium oxide (D_2O) mixtures of limited miscibility with the lower critical consolute temperature*. European Physical Journal E (2022).
   IF =1.89, pkt MEiN = 40
3. J. Kalabiński, A. Drozd-Rzoska, S.J. Rzoska, *Phase equilibria and critical behavior in nematogenic MBBA – isooctane monotectic-type mixtures.* International Journal of Molecular Sciences (2023).
   IF = 6.208, pkt MEiN = 140
4. A. Drozd-Rzoska, S. J. Rzoska, J. Kalabiński, *Impact of Pressure on Low-Molecular Weight Near-Critical Mixtures of Limited Miscibility.* ACS Omega (2020).
   IF = 4.1, pkt MEiN = 70
5. J. Kalabiński, A. Drozd-Rzoska, S. Starzonek, S.J. Rzoska, *Pre-Critical and Giant Post-Freezing and Pre-Melting Effects for Dielectric Properties in a Binary Mixture of Limited Miscibility*. Crystals (2024).
   IF = 2.4, pkt MNiSW = 70
6. J. Kalabiński, A. Drozd-Rzoska, S.J. Rzoska, *Giant premelting effects for solid-liquid discontinuous transition in nitrobenzene under compression*. Crystals (2023).
   IF = 2.4, pkt MNiSW = 70

Nobel Prize winners in the area of dissertation research

The Physics of Critical Phenomena deals with the unique pretransitional/precritical description of physical properties in the broad surrounding of the critical point. Such changes are inherently associated with multimolecular critical fluctuations, dominated sub- and supercritical domains.

Lev D. Landau - (1962) pointed out the role of symmetry and the order parameter for continuous phase transitions.

Kenneth G. Wilson - (1982) award for ‘the theory of critical phenomena in phase transitions’, in particular showing the role of critical exponents with values depending only on the dimensions of the order parameter space. This is the informal beginning of Critical Phenomenon Physics.

Pierre G. de Gennes - (1991) for ‘the discovery that the methods developed in the study of order phenomena in simple systems can be generalized to more complex forms of matter, for example liquid crystals and polymers.’

David J. Thouless, Duncan Haldane, John M. Kosterlitz - (2016) award for ‘theoretical discoveries in the field of topological phase transitions and topological phases of matter’

Motivation - research gaps

- Solutions with limited miscibility are one of the core areas of physical chemistry, critical phenomena physics and related materials engineering issues
- Despite the long history of research into the above-mentioned systems, no method has yet been developed that would allow convenient determination of phase coexistence curves and critical parameters, nor have concepts for such research systems emerged, with the result that :
  - precise characterisations are still lacking even for such basic systems as solutions with an upper critical point, and there are virtually no characterisations for systems with a lower critical point
  - a fundamental problem is the conclusive negation of the Cailletet - Mathias law (rectilinear diameter law) by Rowlinson, in 1986
  - there are limited experimental data on the influence of pressure on critical parameters, which limits the possibilities for reliable discussion and modelling.

This dissertation proposes to fill the aforementioned research gap, starting with the presentation of the author's method for testing solutions with limited miscibility, and continuing with the presentation of new results obtained based on the developed research technique and complementary methods.

Dissertation objectives

Development of the innovative experimental set-up for studying phase equilibria in mixtures of limited miscibility and its applications

Secondary objectives:

- Studies of the impact of temperature and pressure on phase equilibria in selected mixtures of limited miscibility
- New protocols and results for phase equilibria - binodals
- Supplementary broad band dielectric studies, extending the insight
- Studies of monotectic phase equilibria in unique system composed of a liquid crystalline compound (MBBA) and a solvent (isooctane)

Scope

Implementation of a qualitatively new experimental set-up for determining phase equilibria in mixtures of limited miscibility

1. Construction of the experimental setup
2. Design of a methodology to analyze the data obtained in the experiment
3. Validation studies

Investigations of phase equilibria in selected mixtures of limited miscibility, to fill in significant cognitive gaps in results reported so far.

Supplementary studies pretransitional properties using dielectric methods:

1. BDS - *Broadband Dielectric Spectroscopy*
2. NDE - *Nonlinear Dielectric Effect*
3. BDS – insigth under high pressures

[1] S. J. Rzoska, J. Kalabiński, A. Drozd-Rzoska. Fluid Phase Equilibria (2021)

It is shown that the **concentration (isothermic) evolution of the meniscus height is described by straight lines with the temperature-dependent slope. The intersection of such lines determines the critical concentration**.

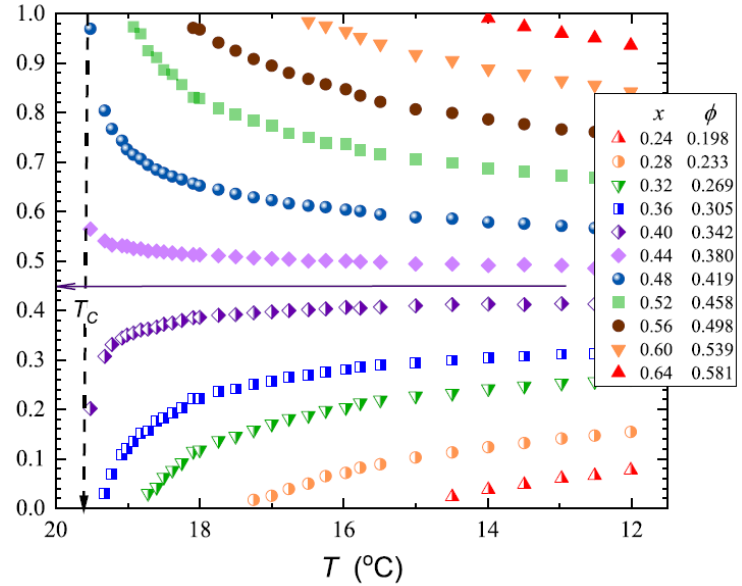
This is a new and qualitatively simpler alternative to the previous technique based on the 'Cailletet-Mathias law'.

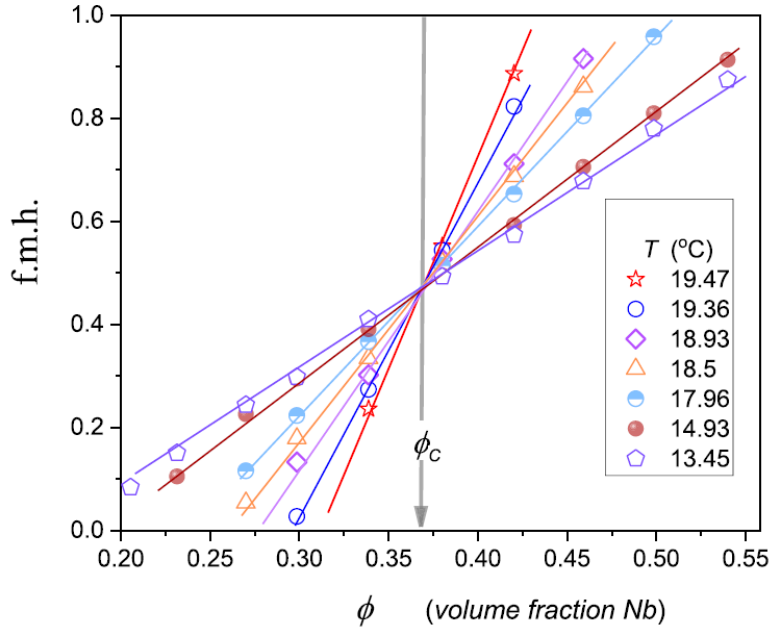
At a minimum, it is only necessary to determine the position of the meniscus for 2 solutions of different concentrations at any 2 temperatures.

It is not only a faster and more accurate method, but also an offer for a simple and automated device for the rapid determination of phase equilibrium parameters

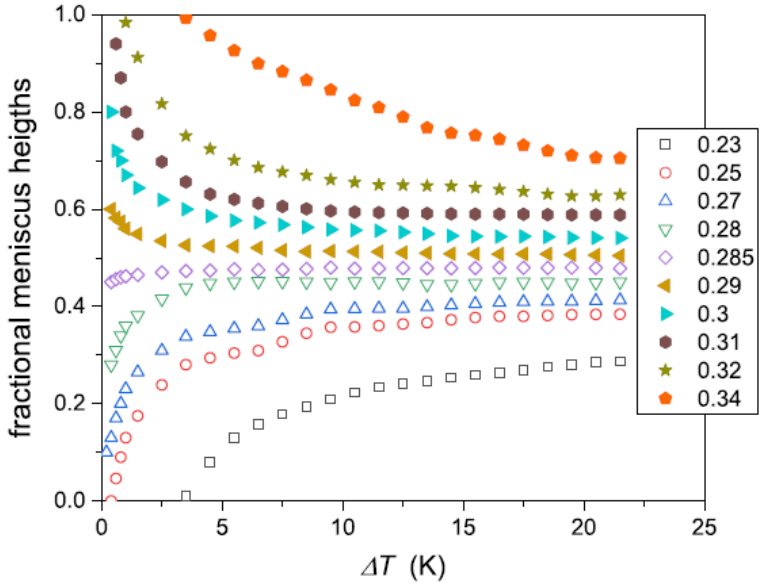
$$h_{i,j}(\varphi, T = const) = \frac{\varphi_{i,j} - \varphi^U}{\varphi^L - \varphi^U} = \frac{\varphi_{i,j}}{\varphi^L - \varphi^U} - \frac{\varphi^U}{\varphi^L - \varphi^U} = A\varphi_{i,j} + a$$

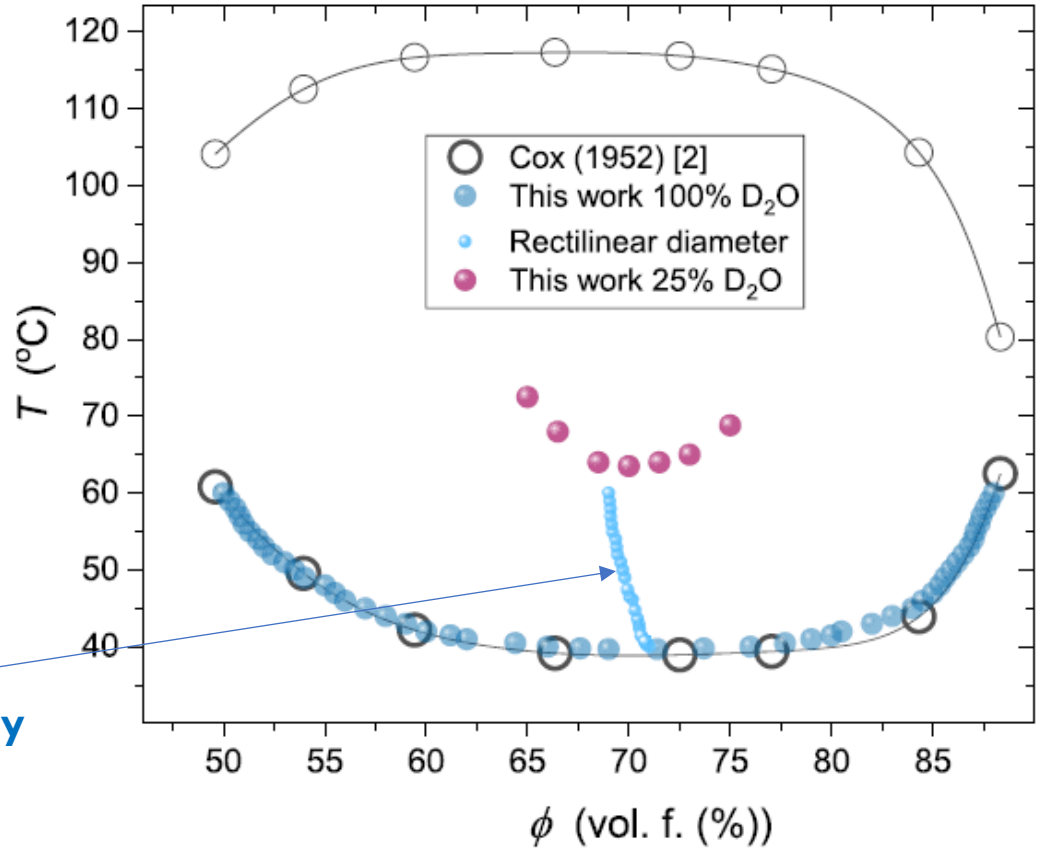
The slope change analysis determines the critical temperature and the exponent β describing the shape of the binodal.





[2] J. Kalabiński, A. Drozd-Rzoska, S. J. Rzoska,. European Physical Journal E (2022).

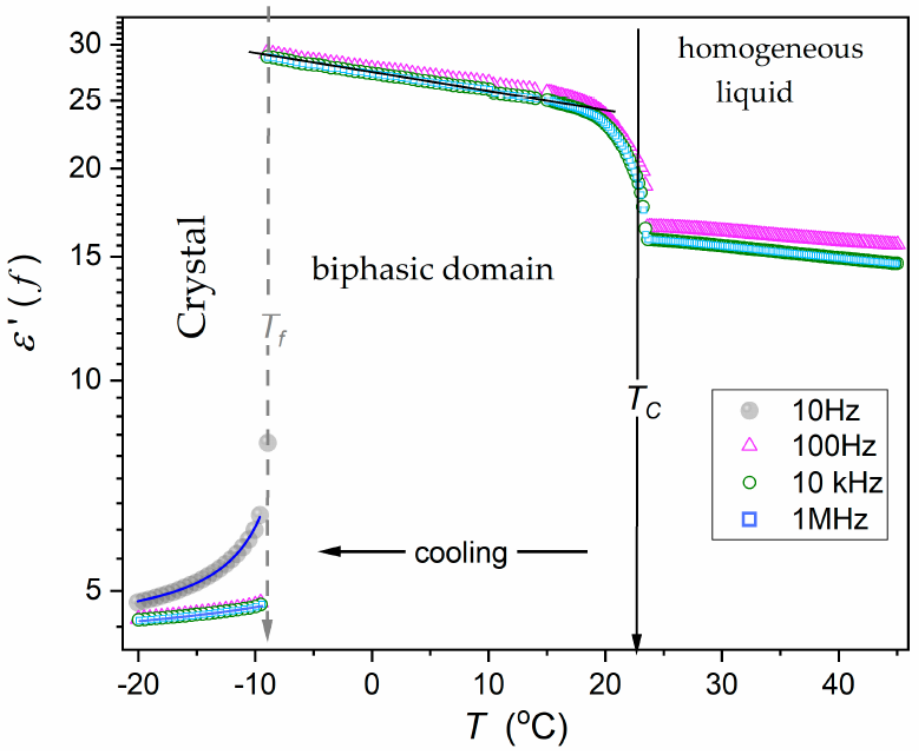




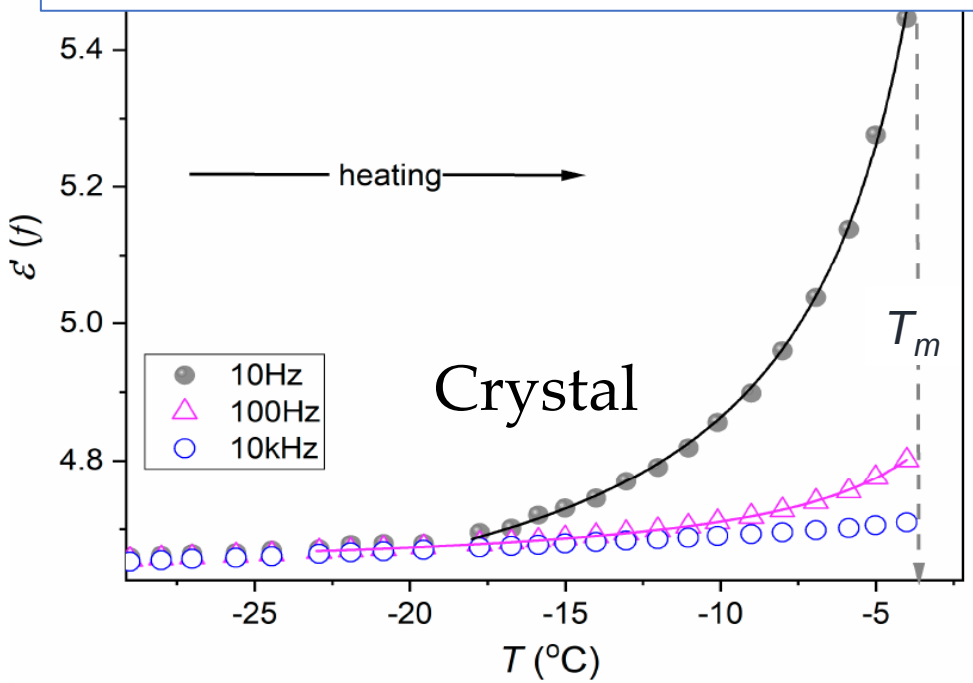
Binodal diameter anomaly

Using the above methodology and the **equipment developed as part of the dissertation, the first accurate data describing the binodal in a Lower Critical Solution Temperature** (LCST) system were obtained. This remarkable state was observed in 3-picoline - D_2O ('heavy water') solutions.

[5] J. Kalabiński, A. Drozd-Rzoska, S. Starzonek, S. J. Rzoska, Crystals (2024).



Premelting effect for the discontinuous Crystal - Liquid phase transition, when heating from the solid phase, in the direction of the melting point



For the solid phase, a qualitatively new, not possible to predict at the research planning stage, result was obtained: a strong critical-like pre-melting changes in the solid Crystal phase.

It can be expressed by the following relation:

$$\varepsilon(T) = C + \frac{A}{T^* - T}$$

where T^* is the extrapolated in the crystalline phase, away from the melting phase transition.

Summary

The innovative apparatus for studying o phase equilibria in mixture with limited miscibility has been built [1], namely:

- ✓ **A new ‚technique'** for determining critical concentrations was proposed **[1]**
- ✓ **For the first time,** accurate data describing the binodal in a lower critical point system have been obtained **[2]**
- ❑ **A new method** of differential analysis of the order parameter has been proposed allowing the precise determination of the critical exponent β **[2]**
- ❑ **For the first time,** a binodal diameter analysis was performed for a system with a lower critical point **[2]**
- ❑ **For the first time,** the monotectic characterization of the isooctane - MBBA system was shown **[3]**
- ❑ **The first record** of the critical opalescence for phase equilibrium in the TP1 region of the isooctane-MBBA system was produced **[3]. It is associated with solvent dominant (isooctane) and liquid crystal dominant (MBBA) phases equilibria.**

Complementary studies carried out, with which:

- ❑ **For the first time,** data were obtained that allowed the analysis of the shape of the binodals under pressure in the nitrobenzene-decane system **[4]**
- ✓ **For the first time,** a strong premelting effect was observed in the solid phase for nitrobenzene - decane critical solution **[5]**
- ❑ **For the first time,** a critical premelting effect was shown for the melting / crystallization discontinuous transition in pure nitrobenzene **[6]**