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Mesoscopic Structures in HFIP/H₂O based Elektrolytes
Monotony and Oscillatory Correlations vs. Cluster Formation

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Abstract

This thesis investigates the formation of microheterogeneities and phase separation phenomena in binary solvent mixtures of hexafluoroisopropanol (HFIP) and water, with a particular focus on the role of fluorinated acids and antagonistic salts. The study is motivated by previous reports of nanostructural organization in polar solvent systems containing salts with asymmetric solvation preferences.

Small-angle X-ray scattering (SAXS) measurements were carried out using a Bruker AXS Nanostar instrument to characterize the temperature-dependent structural behavior of HFIP–water mixtures and their modifications upon addition of pentafluoropropionic acid, tetraphenylphosphonium chloride (TPhP^+Cl^-), and sodium tetraphenylborate (NaBPh_4). Complementary techniques such as attenuated total reflectance (ATR) spectroscopy and pH measurements were used to analyze changes in molecular interactions and sample stability.

The results show that pure HFIP-water mixtures display critical scattering consistent with Ornstein-Zernike behavior, with correlation lengths increasing near the critical composition. The addition of fluorinated acids strongly reduces the pH, increases proton concentration, and induces additional hydrogen-bonding interactions, which in turn influence the scattering profiles. Antagonistic salts introduce ion-specific effects that significantly alter the phase behavior.

Taken together, this work highlights the sensitivity of HFIP-water mixtures to ionic perturbations and provides a framework for understanding how fluorinated acids and antagonistic salts modulate critical fluctuations, hydrogen-bonding networks, and nano-scale structure. The findings may offer broader implications for the design of solvent systems with tunable self-assembly and phase behavior in soft matter and supramolecular chemistry.

Kurzfassung

Diese Arbeit untersucht die Bildung von Mikroheterogenitäten und Phasentrennungssphänomenen in binären Lösungsmittelsystemen aus Hexafluoroisopropanol (HFIP) und Wasser, mit besonderem Fokus auf den Einfluss fluorierter Säuren und antagonistisch wirkender Salze. Die Motivation der Studie basiert auf früheren Berichten über nanostrukturelle Organisation in polaren Lösungsmittelsystemen, die Salze mit asymmetrischen Solvatisierungseigenschaften enthalten.

Zur Charakterisierung des temperaturabhängigen Strukturverhaltens von HFIP–Wasser-Mischungen sowie deren Modifikationen durch Zugabe von Pentafluorpropionsäure, Tetraphenylphosphonium Chlorid (TPhP^+Cl^-) und Natrium Tetraphenylborat (NaBPh_4) wurden SAXS Messungen an einer Bruker AXS Nanostar-Anlage durchgeführt. Ergänzend kamen ATR Spektroskopie und pH-Messungen zum Einsatz, um Veränderungen der molekularen Wechselwirkungen und der Probenstabilität zu analysieren.

Die Ergebnisse zeigen, dass reine HFIP-Wasser-Mischungen ein kritisches Streuverhalten aufweisen, das dem Ornstein-Zernike-Modell entspricht, wobei die Korrelationslängen nahe der kritischen Zusammensetzung anwachsen. Die Zugabe fluorierter Säuren führt zu einer starken Absenkung des pH-Wertes, zu einer erhöhten Protonenkonzentration und zu zusätzlichen Wasserstoffbrückenbindungen, welche die Streuprofile maßgeblich beeinflussen. Antagonistische Salze erzeugen ionenspezifische Effekte, die das Phasenverhalten signifikant verändern.

Zusammenfassend verdeutlicht diese Arbeit die hohe Sensitivität von HFIP-Wasser-Systemen gegenüber ionischen Störungen und liefert ein Rahmenwerk zum Verständnis, wie fluorierter Säuren und antagonistische Salze kritische Fluktuationen, Wasserstoffbrückennetzwerke und Strukturen im Nanometerbereich modulieren. Die Ergebnisse eröffnen mögliche Perspektiven für die Gestaltung von Lösungsmittelsystemen mit gezielt einstellbarem Selbstorganisations- und Phasenverhalten in der weichen Materie und Supramolekularchemie.

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1. Introduction

The study of microheterogeneities in liquid mixtures has a long tradition in physics and chemistry, dating back to early investigations into phase behavior and molecular organization in binary solvent systems in the late 19th and early 20th centuries. The development of scattering techniques such as small-angle X-ray scattering (SAXS) in the mid-20th century provided a tool to probe nanoscale structure in liquids. These techniques made it possible to detect subtle density fluctuations and nanostructured domains in complex fluids, laying the foundation for modern studies of self-organization in solvent mixtures.[14] Building on this historical background, recent research has increasingly focused on solute-induced structural heterogeneities in polar solvent mixtures. In particular, studies of acetonitrile (ACN)-water systems containing so-called antagonistic salts, ions with opposing solvation preferences, have shown that such additives can drive the formation of nanoscopic domains. These heterogeneities, detectable by SAXS, arise from ion-solvent interactions that modulate local structure and provide new insight into how microscopic forces shape macroscopic solution behavior. [5]

Inspired by these findings, this Master’s thesis investigates the formation of microheterogeneities in binary solvent systems composed of hexafluoroisopropanol (HFIP) and water. HFIP was selected due to its unique physicochemical properties. It is a highly polar, hydrogen-bonding, and fluorinated solvent often described in the literature as a “highly versatile solvent.” Its amphiphilic character allows it to engage simultaneously in hydrophilic and hydrophobic interactions, making it particularly sensitive to structural perturbations and thus well suited for exploring solute-driven nanoscale organization.[10] The central focus of this work is to examine whether fluorinated acids can induce microheterogeneities in HFIP-water mixtures in a manner comparable to previously reported HFIP-water-amide systems. While amides interact with HFIP primarily through neutral dipolar interactions, fluorinated acids introduce ionic dissociation and fluorophilic effects, thus combining electrostatic contributions with non-covalent interactions in the same solvent environment. Comparing these two additive classes provides an opportunity to disentangle the relative roles of ionic versus dipolar interactions in driving nanoscale structural organization.[10]

Fluorinated acids are particularly relevant in this context because they combine strong Brønsted acidity with highly electronegative, partially hydrophobic fluorinated anions. Upon dissociation, these acids supply both charge carriers and fluorinated species that interact with HFIP through hydrogen bonding, ion-dipole interactions, and fluorophilic effects. Structurally, they share important characteristics with amides, such as polar functional groups and partial electron delocalization, enabling comparable non-covalent interactions with the solvent matrix. However, unlike amides, acids dissociate and generate local charge inhomogeneities, which may more effectively trigger the formation of

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microheterogeneous domains.[2]

The objectives of this thesis are therefore threefold. First, to investigate whether fluorinated acids can induce microheterogeneities in HFIP-water mixtures that are detectable by small-angle X-ray scattering. Second, to compare these results with previously studied HFIP-amide systems in order to differentiate the effects of ionic dissociation from neutral dipolar interactions. Third, to characterize the resulting nanoscale structural organization as a function of solvent composition and additive type. By addressing these aims, this work seeks to advance the understanding of solute-driven nanostructuring in fluorinated solvent systems and contribute to the broader study of self-organization phenomena in liquid mixtures.

2. Theory

This first part outlines the theoretical foundations necessary for understanding the phenomena and experimental methods addressed in this work. It begins with the principles of X-ray scattering, focusing on small angle (SAXS) and wide angle X-ray scattering (WAXS) as tools for probing structures from the atomic to the mesoscale. The discussion then introduces key concepts from soft matter physics, particularly the behavior of amphiphilic compounds and their ability to self-assemble into ordered mesophases. Furthermore, the thermodynamics of phase separation is examined, including its description through the Ornstein-Zernike theory, which relates scattering intensity to correlation functions and captures the role of critical fluctuations near phase transitions. The scaling behavior of these fluctuations, characterized by critical exponents, is also addressed to provide a deeper understanding of how molecular interactions give rise to structural heterogeneities.

2.1. X-Ray Scattering

The foundation of X-ray based structural analysis was laid in 1895, when Wilhelm Conrad Röntgen discovered a previously unknown form of electromagnetic radiation. In his seminal publication Röntgen described the emission of highly penetrating rays from a cathode-ray tube-radiation that could pass through solid matter and expose photographic plates. [40]

X-ray radiation is a form of electromagnetic radiation with wavelengths ranging from 0.01 nm to 10 nm, corresponding to photon energies from 0.1 keV to over 100 keV. Due to this wavelength regime, X-rays are particularly suitable for probing structures at atomic length scales.[20]

An advancement in the understanding of X-rays occurred in 1912, when Max von Laue, together with Walter Friedrich and Paul Knipping, experimentally demonstrated the diffraction of X-rays by crystalline materials. This provided direct evidence for the wave nature of X-rays and simultaneously revealed the periodic arrangement of atoms within crystals. From these findings, von Laue derived the Laue conditions that govern the constructive interference of scattered X-rays in periodic structures.[17]

The interaction of X-rays with matter is primarily governed by their scattering from electrons surrounding the atomic nuclei. In the case of elastic scattering, the energy and wavelength of the incident photon remain unchanged, only its direction is altered. This elastic scattering leads to interference patterns that contain information about the spatial distribution of the electron density $\rho_e(\mathbf{r})$ within the sample.

In X-ray scattering, the scattering length density $\rho(\mathbf{r})$ is directly related to the electron density $\rho_e(\mathbf{r})$ through the mass density $\rho_m(\mathbf{r})$. The electron density can be calculated

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using the mass density and the number of electrons per unit mass, denoted as Z_m .

$$\rho_e(\mathbf{r}) = \rho_m(\mathbf{r})Z_m \quad (2.1)$$

By multiplying equation 2.1 with the Thomson scattering length $r_e = \frac{e^2}{4\pi\epsilon_0 mc^2}$ one obtains the scattering length density.[12]

$$\rho(\mathbf{r}) = r_e \rho_m(\mathbf{r})Z_m = \frac{e^2}{4\pi\epsilon_0 mc^2} \rho_e(\mathbf{r}) \quad (2.2)$$

The physical relevance of r_e becomes apparent in the Thomson cross section, which quantifies the elastic scattering from a single free electron. For unpolarized radiation, the differential cross section is

$$\left(\frac{d\sigma}{d\Omega}\right)_T = \frac{r_e^2}{2} (1 + \cos^2 \theta), \quad (2.3)$$

where θ being the scattering angle. Integration over all solid angles yields the total Thomson cross section

$$\sigma_T = \frac{8\pi}{3} r_e^2. \quad (2.4)$$

In the context of amorphous material, the scattering length density is most conveniently expressed in terms of the real part of the atomic form factor $f_1(\mathbf{q}, E)$ rather than the bare atomic number Z_m . While Z_m reflects only the number of electrons, f_1 additionally includes the $\mathbf{q}$ -dependence of the atomic form factor and the energy-dependent dispersion corrections. In practice, the contrast is therefore governed by differences in f_1 between distinct regions of the sample, which makes f_1 the physically relevant parameter.[26]

For example the f_1 value of fluorine for $E = 8.45 \text{ keV}$ is $f_1 = 9.07041 \text{ e}^- \text{atom}^{-1}$. In comparison the Z -value of fluorine is $Z = 9 \text{ e}^- \text{m}_{\text{unit}}^{-1}$. [34]

Owing to this proportional relationship, the subsequent calculations of the scattering intensities are, without loss of generality, performed using the scattering length density. This section is written after the results of Gross and Marx in [20], but in a more general way via the f_1 value. For a measurement with constant energy E , the energy dependency can be neglected. In contrast to crystalline systems, amorphous materials do not exhibit a periodic lattice. Therefore, the scattering length density $\rho(\mathbf{r})$ is described directly by the contributions of the atoms located at positions $\mathbf{r}_j$. Each atom contributes with its atomic form factor $f_{1,j}$, which corresponds to the real part of the complex form factor and includes both the q -dependence and the energy-dependent dispersion corrections. The scattering length density can thus be written as

$$\rho(\mathbf{r}) = r_e \sum_j f_{1,j}(\mathbf{q}, E) \delta(\mathbf{r} - \mathbf{r}_j). \quad (2.5)$$

From this expression, the scattering amplitude $F(\mathbf{q})$ is obtained by taking the Fourier transform of $\rho(\mathbf{r})$,

$$F(\mathbf{q}) = \int_V \rho(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} = r_e \sum_j f_{1,j}(\mathbf{q}, E) e^{i\mathbf{q}\cdot\mathbf{r}_j}. \quad (2.6)$$

2.1. X-Ray Scattering

The non resonant form factor $f_{1,j}$ for free electrons $E \rightarrow \infty$ itself is defined as the Fourier transform of the electron density distribution $\rho_j(\mathbf{r})$ of atom j ,

$$f_{1,j}(\mathbf{q}) = \int_V \rho_j(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}. \quad (2.7)$$

Finally, the intensity observed in a SAXS experiment is proportional to the square of the scattering amplitude,

$$I(\mathbf{q}) \propto |F(\mathbf{q})|^2 = \left| r_e \sum_j f_{1,j}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}_j} \right|^2. \quad (2.8)$$

This formulation makes clear that the measured intensity originates from spatial fluctuations of the electron density. These fluctuations are weighted by the real part of the atomic form factor f_1 , rather than by the bare atomic number Z_m , and therefore provide direct information about nanostructural contrast in amorphous systems.

The scattering vector $\mathbf{q}$ is defined via the difference of the transmitted $\mathbf{k}_{tr}$ and scattered $\mathbf{k}_{sc}$ wavevector. [20]

$$\mathbf{q} = \mathbf{k}_{tr} - \mathbf{k}_{sc} \quad (2.9)$$

Due to both having a magnitude of $\frac{2\pi}{\lambda}$, where θ is half the scattering angle the magnitude of $\mathbf{q}$ is defined as [12]

$$|\mathbf{q}| = \frac{4\pi}{\lambda} \sin(\theta) \quad (2.10)$$

Figure 2.1 presents a schematic representation of a typical X-ray scattering setup, designed to probe the internal structure of materials by analyzing the scattering of X-rays upon interaction with matter. The setup generally comprises three main components: an X-ray source, a sample environment, and a detection system.

At the beginning of the beam path, a monochromatic X-ray beam is generated, typically using either a sealed X-ray tube or a synchrotron radiation source. The beam is collimated and directed onto the sample, where it interacts with the material's internal structure. Depending on the experimental geometry, the scattered X-rays $\vec{k}_{sc}$ are emitted at various angles 2θ relative to the incident beam. Additionally, Figure 2.1 includes the transmitted wave vector $\vec{k}_{tr}$, which represents the non-deflected part of the beam passing directly through the sample. The scattering vector $\vec{q}$ is also shown to illustrate the scattering condition described in Equation 2.9.

The scattered intensity is captured by a position-sensitive detector, which is placed at a defined distance x from the sample. This detector covers a specific angular range and allows for the spatially resolved measurement of scattering patterns.[12]

The scattering pattern encodes information about the spatial distribution of electron density within the material. From this, one can derive structural features such as lattice constants, particle sizes, shapes, or electron density fluctuations.

To ensure high data quality, setups include beam conditioning optics like for example

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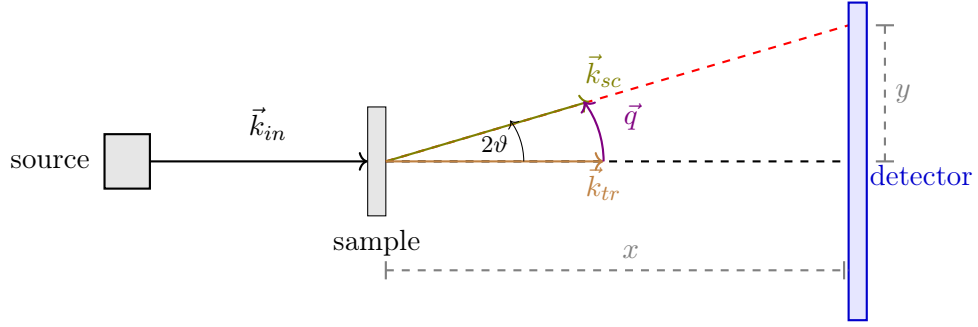


Figure 2.1.: Scattering geometry of a general X-ray setup, where $\vec{k}_{sc}$ denotes the wave vector of the scattered beam, $\vec{k}_{tr}$ represents the wave vector of the transmitted beam, $\vec{k}_{in}$ the incoming beam and $\vec{q}$ corresponds to the scattering vector. For the magnitudes the following holds: $|\vec{k}_{sc}| = |\vec{k}_{tr}| = |\vec{k}_{in}|$. The parameter x denotes the distance between the sample and the detector, while y represents the separation between the transmitted and scattered beams on the detector plane.

slits, sample positioning systems, and vacuum chambers.[12]

X-ray scattering provides a versatile framework to probe structural information across a wide range of length scales. While small-angle X-ray scattering (SAXS) is particularly sensitive to larger structural features on the nanometer to mesoscale range and wide-angle scattering (WAXS) primarily reveals atomic arrangements and short-range order. In the following, the focus will be placed on SAXS, as it represents a method to investigate microstructural organization, phase separation, and heterogeneities in soft matter systems.

2.2. Small Angle X-ray Scattering (SAXS)

Small-Angle X-ray Scattering (SAXS) is a common method to analyse nanostructured materials. The measurements contain information about the particle size and their distribution from 1 nm up to 100 nm. The typical angular range which a SAXS can measure is from $q = 0.08 \text{ nm}^{-1}$ up to $q = 3 \text{ nm}^{-1}$. Physically, the SAXS signal arises from the coherent superposition of X-rays scattered by regions with differing electron density. The resulting angular scattering distribution $I(q)$ provides information about the shape, size, and other structure information in this range of size. [21]

Amorphous Materials do in general not have any long range orders, like crystals. With SAXS measurements it is still possible to gain information about diffraction features. A typical material which is measured with SAXS, are solutions with different components. [21]

For SAXS measurements, a highly collimated and well-defined X-ray beam is essential. Additionally, unwanted scattering must be minimized or eliminated. Altogether, this highlights the importance of beam collimation quality in SAXS experiments.[9] Figure 2.2

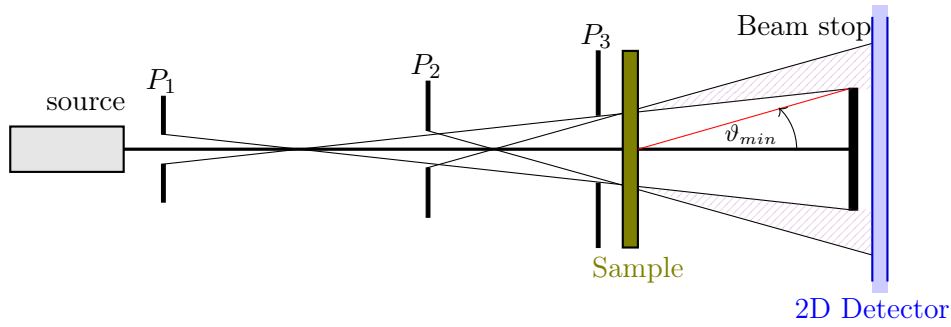


Figure 2.2.: Collimation system with 3 pinholes P_i for a SAXS setup. The beam paths are indicated with black thin lines. ϑ_{min} is the minimum angle which can be reached without a problem with unwanted scattering. The violet schraffier regions are the regions where pinhole scattering occurs. The sketch is designed after the work of [9] and [21]

shows a typical pinhole collimation setup for SAXS setup. It contains three pinholes, a beamstop and a 2D Detector. The first two pinholes in Figure 2.2 define the beam, while the third one remove the unwanted scattering from edges from pinholes one and two.[12] Small angle X-ray scattering (SAXS) is powerful for the investigation of systems whose characteristic structural features lie on the nanometer to micrometer scale. This makes it especially suitable for the study of so called soft matter, a broad class of materials that includes polymers, surfactants and liquid crystals. In such systems, the balance between enthalpic interactions and entropic contributions often leads to self-organization and the emergence of complex hierarchical structures. SAXS provides direct access to these structural features by probing density fluctuations and spatial correlations, thereby linking microscopic organization with macroscopic material properties. In the following, the fundamental aspects of soft matter and its relevance to amphiphilic systems and phase behavior will be discussed.

2.3. Soft Matter

Soft matter refers to a broad class of materials that are easily deformable under external forces, thermal fluctuations, or due to self-organization. Examples include colloids, polymers, liquid crystals, amphiphiles, and surfactants, among many others. What these systems share is that their structural building blocks are generally larger than atoms or simple molecules, often ranging from nanometers to micrometers in size.[14]

While individual surfactant molecules and liquid crystal mesogens are not large themselves, they can spontaneously organize into extended structures, such as micelles, lamellae, or mesophases, that behave collectively as larger functional units. Surfactants, in particular, form specific types of micelles depending on molecular geometry and environmental conditions. These will be described in more detail in the following section. [14]

Unlike crystalline solids, soft matter systems are typically disordered or only partially

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ordered. They exhibit a rich variety of mesoscopic structures, governed by a delicate balance of entropic and enthalpic interactions. This results in phenomena such as phase separation, self-assembly, micellization, and spontaneous symmetry breaking.[14]

They can be distinguished between two characteristic classes of soft matter behavior. First in materials that exhibit large and nonlinear responses to external stimuli, where the relationship between stress and strain cannot be described by linear elasticity. And second in systems with slow and non-equilibrium dynamics, where the response time becomes so long that the system is effectively trapped in a metastable state. [14]

Furthermore, due to their sensitivity to external conditions such as temperature, concentration, or pH soft matter systems often show complex phase behavior, including transitions between isotropic, lamellar, hexagonal, or bicontinuous cubic phases. Their capacity to form self-organized nanostructures makes soft matter highly relevant for materials science.[14]

From an experimental perspective, X-ray and neutron scattering techniques are especially powerful for characterizing soft matter, as they allow access to structural information on length scales ranging from nanometers to micrometers—without damaging the sample.[21] In this work, a surfactant with amphiphilic character is used. To better understand its structural properties and behavior, the following section provides a more detailed overview of this specific class of soft matter.

2.4. Amphiphilic compounds

The term amphiphile originates from the ancient Greek words $\alpha\mu\phi\iota$ (amphi), meaning 'both', and $\varphi\iota\lambda\omicron\varsigma$ (philos), meaning 'loving'. This etymology reflects the dual nature of amphiphilic molecules, which contain two chemically distinct regions within the same molecular structure, a hydrophilic and a hydrophobic part. Because of this duality, amphiphiles are also commonly referred to as surfactants.[37] Structurally, amphiphilic molecules typically consist of a polar head group that is hydrophilic and interacts favorably with aqueous environments, and a nonpolar tail that is hydrophobic and tends to avoid contact with water, preferring interaction with oils or other nonpolar substances.[42]

Despite being covalently connected, the polar and nonpolar segments of an amphiphilic molecule exhibit fundamentally different chemical affinities. This internal incompatibility is the driving force behind a wide range of self-assembly phenomena, such as micelle formation, bilayer membranes, or phase separation in aqueous environments. Amphiphiles reduce the interfacial tension between polar and nonpolar phases and are thus essential components in detergents, emulsifiers, and many biological systems. Their ability to simultaneously interact with water and oil phases makes amphiphiles particularly important in soft matter and colloid science.[42]

Figure 2.3 shows a generic phase diagram of an amphiphilic surfactant in aqueous solution. Including different phases depending on the percentage of water and the surfactant. Figure 2.4 shows blender images corresponding to the different main phases in Figure 2.3. The images are performed after the work of Seddon mentioned in his paper from 1990 [41].

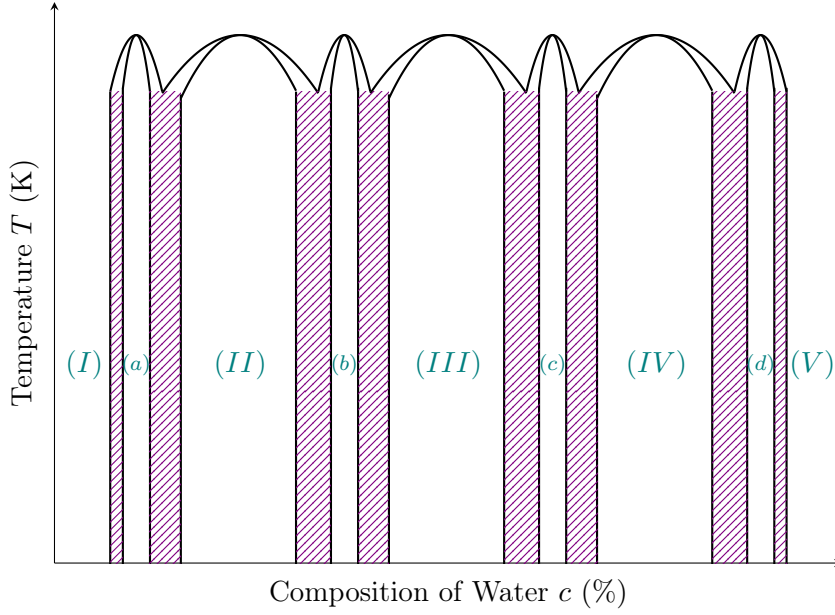


Figure 2.3.: Generic phase diagram of a surfactant–water system, adapted from Seddon.[41] The diagram illustrates a characteristic phase behavior of surfactants in aqueous solution. The main phases are labeled (I) through (V), while the intermediate phases are indicated by (i) through (iv).

2.5. Self-Assembling

Self-assembly is a fundamental phenomenon by which individual molecules or particles spontaneously organize into ordered structures through the interplay of thermodynamic driving forces and non-covalent interactions. Physically, the process follows from the system’s tendency to lower its Gibbs free energy, balancing enthalpic stabilization and entropic effects.

$$G = H - TS, \quad (2.11)$$

Where H is the enthalpic, S corresponds to the entropy and T is the temperature. Attractive interactions such as hydrogen bonding, van der Waals forces, electrostatics typically lower the enthalpic term H . At the same time, entropy S may increase due to the release of solvent molecules, counterions, or the gain in configurational freedom of surrounding species. [4] The balance between these opposing factors drives the spontaneous formation of ordered assemblies, ranging from simple micelles to complex supramolecular architectures.[3]

A hallmark of self-assembly is its cooperative nature. Once a critical concentration or threshold condition is exceeded, small local fluctuations become amplified, and the system reorganizes into a more stable, structured phase. This behavior is often analogous to phase transitions and can be described using concepts from statistical mechanics, including correlation functions and order parameters.[37]

2. Theory

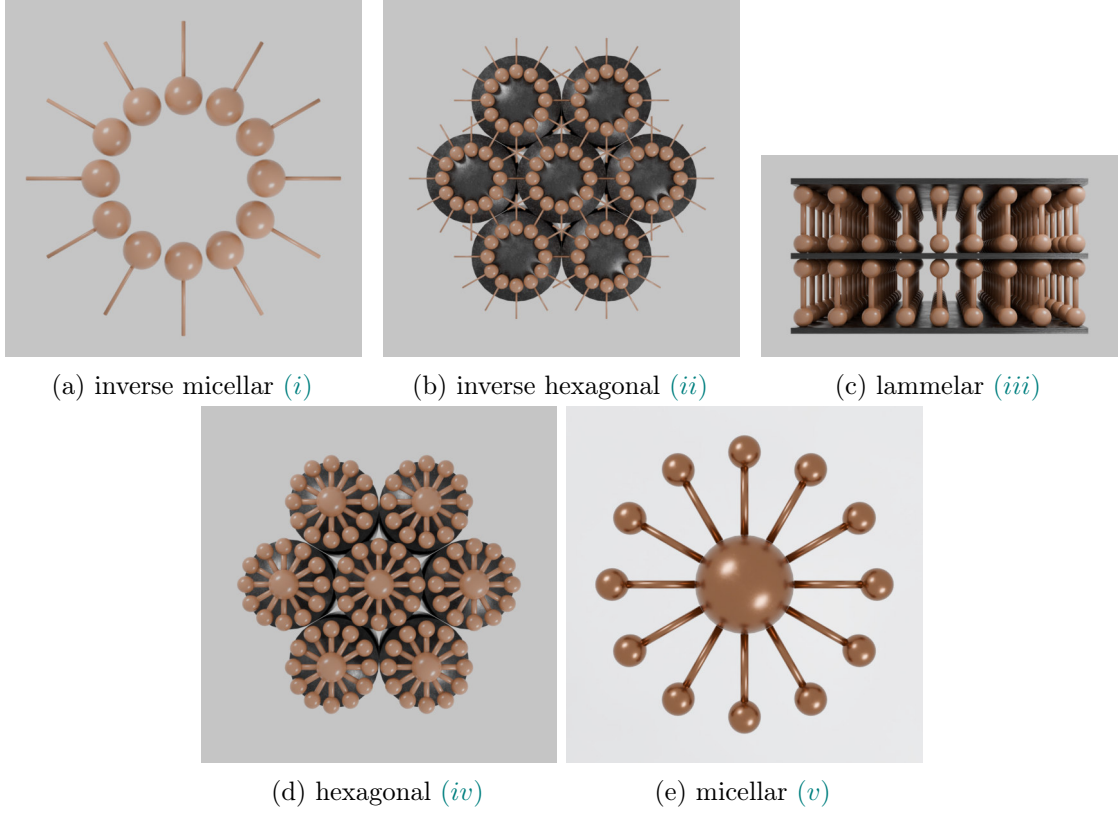


Figure 2.4.: Generic representation of the phases in diagram Figure 2.3. The images were performed in Blender after the work of Seddon [41]

On larger length scales, self-assembly frequently results in periodic structures with characteristic domain sizes. These periodicities can be directly probed by scattering techniques such as small-angle X-ray scattering (SAXS) or small-angle neutron scattering (SANS), which provide information on correlation lengths, structural symmetry, and internal organization.[12]

In soft matter systems, amphiphilic molecules are a prototypical class of self-assembling compounds. Due to their inherent separation into hydrophilic and hydrophobic segments, they exhibit rich phase behavior and can form a variety of lyotropic liquid crystalline phases, including micellar, hexagonal, lamellar, and cubic arrangements Figure 2.4[12]. The specific phase formed depends sensitively on experimental parameters such as concentration, temperature, and solvent polarity. Subtle changes in these conditions can induce transitions between different morphologies, allowing precise control over self-assembled structure.[14]

2.6. Mechanism of phase separation

Gibbs distinguished between two types of concentration fluctuations that can lead to the formation of new stable phases. The first type is characterized by small spatial dimensions but large changes in concentration, and is associated with nucleation processes, which will not be addressed in this work. The second type involves fluctuations that are spatially extended but exhibit only small changes in concentration, corresponding to the mechanism of spinodal decomposition. [37]

In order for phase separation to occur, the system must be within the spinodal region of the binary phase diagram. Spinodal decomposition is a process in which a thermodynamically unstable mixture, located within a miscibility gap, can transform into a mixture of two phases. These two phases are close to their equilibrium state. They evolve continuously from the initially uniform mixture through uphill diffusion and do not depend on nucleation events. Uphill diffusion is a gradual and smooth transformation, describing the diffusion from regions of lower concentration to regions of higher concentration. This process primarily occurs in the spinodal region, as even small deviations from uniformity reduce the system's free energy. [1]

Due to the small changes in concentration (amplitude) the Helmholtz free energy can be Taylor expanded to find the free energy of the solution.

$$F(N_p, N_s, T) = V f(c, T) \quad (2.12)$$

While $f(c, T)$ is the Helmholtz free energy per unit volume and V corresponds to the volume as the derivative of Gibbs free energy with respect to the pressure and N_p is the number of polymer molecules and N_s the number of solvent molecules.[14]

To obtain a homogeneous solution through mixing, the free energy density after mixing must be lower than before. This requires the free energy function $f(c, T)$ to be strictly convex, satisfying the following condition

$$f(xc_1 + (1 - x)c_2) < xf(c_1) + (1 - x)f(c_2) \quad (2.13)$$

2. Theory

Where $x \in (0, 1)$ and c_1 and c_2 represent the concentrations of the components before mixing. This inequality is equivalent to the requirement that the second derivative of $f(c, T)$ with respect to c is larger than zero over the interval $[c_1, c_2]$. In other words, $f(c, T)$ is upper concav on this region. This scenario is illustrated in Figure 2.5. Due to the principle of energy minimization, a system located in the unstable region will undergo phase separation into two coexisting phases with concentrations c_1 and c_2 , where the free energy is lower.[14]

Figure 2.5 displays the Helmholtz free energy per unit volume $f(c, T)$ as a function of composition c for a binary system exhibiting a miscibility gap.[37] The concentrations

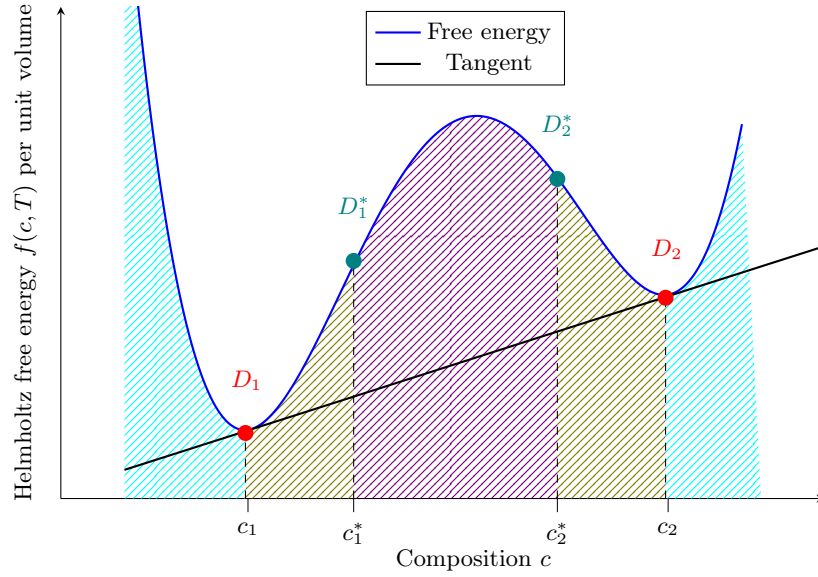


Figure 2.5.: Helmholtz free energy per unit volume as a function of composition c . The concentrations c_1 , c_1^* , c_2^* , and c_2 define regions of stable (cyan), metastable (olive), and unstable (violet) mixture. The tangent touches the curve at the stable phases D_1 and D_2 .

c_1 and c_2 correspond to the points where the common tangent intersects the free energy curve at D_1 and D_2 . These points represent the compositions of the two coexisting phases resulting from phase separation. The corresponding phases have welldefined volumes V_1 and V_2 , and concentrations c_1 and c_2 , respectively.

The concentrations c_1^* and c_2^* denote the inflection points of the free energy curve, where $\frac{\partial^2 f(c)}{\partial c^2} = 0$. These points are indicated by D_1^* and D_2^* and mark the boundaries of the spinodal region. The cyan shaded area indicates the thermodynamically stable region, where the solution remains homogeneous. The green areas represent metastable states, while the violet region corresponds to the unstable regime in which the solution undergoes

2.6. Mechanism of phase separation

phase separation. In both the stable and metastable regions, the second derivative of the free energy $f(c, T)$ with respect to concentration is positive. As a result, small fluctuations in concentration increase the free energy, which suppresses these fluctuations and restores the system to a homogeneous state. In contrast, within the unstable region, the second derivative is negative. Here, any small fluctuation leads to a decrease in free energy, amplifying the deviation and initiating phase separation. A stable two-phase system can form from an unstable state characterized by

$$\frac{d^2 f}{dc^2} < 0 \quad (2.14)$$

This condition defines the onset of spinodal decomposition, as previously discussed. [37] An alternative way to illustrate the mechanism of phase separation is presented in Figure 2.6. This figure shows the phase diagram by plotting the concentration c as a function of temperature T . The binary mixture exhibits a miscibility gap in which two phases can coexist. In Figure 2.6, this miscibility gap is represented by the bold black curve. It also contains a critical point, marked by the red dot. The critical point would not be included in the other representation of phase separation. Spinodal decomposition can occur within the yellow-shaded region, which corresponds to the chemical spinodal. In contrast, the lime green region represents the metastable regime. The boundary between the metastable and unstable regions is defined by the chemical spinodal, which satisfies the following condition.[1]

$$\frac{\partial^2 f}{\partial c^2} = 0 \quad (2.15)$$

This criterion is consistent with the condition for instability discussed in Equation 2.14, as unstable solutions lie below the chemical spinodal.

In binary fluid mixtures, the critical point marks the unique thermodynamic state at which the compositional difference between coexisting phases vanishes and macroscopic phase separation no longer occurs. Near this point, the system is dominated by large-scale concentration fluctuations with a diverging correlation length. The position of the critical point in the phase diagram, characterized by the critical temperature T_c and critical composition c_c , is not fixed, but can be significantly shifted by introducing small amounts of solutes that interact selectively with the solvent components. Chemical additives such as salts, acids, fluorinated alcohols, or amphiphilic molecules can alter intermolecular interactions by modifying hydrogen bonding networks, dielectric properties, or solvation enthalpies. These perturbations influence the effective free energy of mixing, often resulting in a change of miscibility or in the onset of mesoscale structure formation. In ternary systems containing amphiphilic or cosolvating species, such effects can lead to a lowering or elevation of the critical temperature, changes in the curvature of the binodal line, or even the emergence of new critical points. [35]

The schematic phase diagram reproduced from Fisher's work on the decay of correlations in linear systems illustrates the qualitative differences between monotonic and oscillatory decay of correlations in fluids.[16] The diagram plots the density ρ versus the temperature

2. Theory

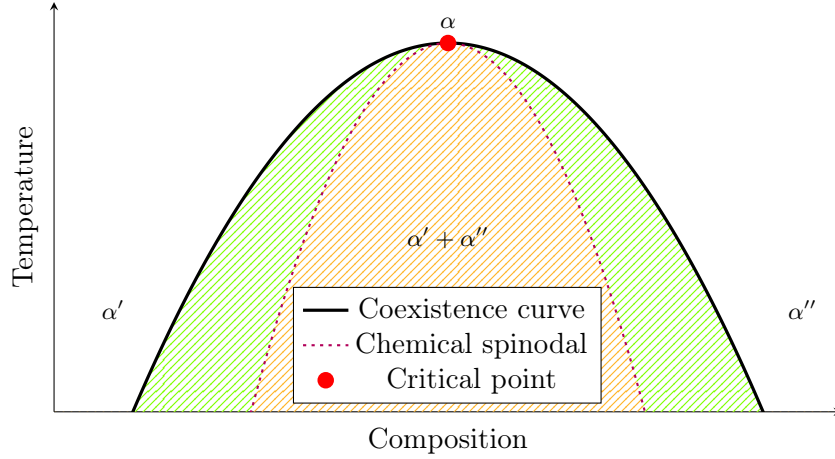


Figure 2.6.: Schematic phase diagram of a binary mixture showing a miscibility gap. The solid line represents the coexistence curve, the dotted line indicates the chemical spinodal, and the red dot marks the critical point. The shaded regions denote areas of metastability and instability.

T , showing the gas, liquid, and solid phases as well as the coexistence curve terminating at the critical point T_c . Below the critical temperature, correlations in the fluid decay in a monotonic fashion, reflecting exponential damping of density fluctuations. However, beyond a certain line, known as the Fisher-Widom line, the decay of correlations changes character and becomes oscillatory, signaling the emergence of structural correlations reminiscent of short-range ordering, typically associated with the liquid phase at higher densities. This line therefore separates regions of different correlation behavior rather than true thermodynamic phases.[16] Fisher’s diagram was fundamental in establishing that correlation decay in fluids is not universally monotonic, but can exhibit damped oscillations depending on the interplay of density, temperature, and intermolecular forces, thus providing the theoretical foundation for later developments in liquid state theory and integral equation approaches.

The schematic phase diagram introduced by Fisher [16] highlights the fundamental distinction between monotonic and oscillatory decay of correlations in fluids. While Fisher’s approach was mainly phenomenological, Kirkwood’s statistical mechanical treatment of liquid solutions [27] provides the microscopic basis for such correlation functions. In his theory, the potential of mean force and corresponding distribution functions are derived from the canonical ensemble, explicitly linking intermolecular forces to measurable thermodynamic quantities. This framework emphasizes the role of electrostatic and dipolar interactions in determining the effective pair correlations in solution. In particular, Kirkwood showed that the decay of correlations can be captured through integral equations for the potential of average force, which in certain regimes reduce to simple exponential laws, while in others more complex (oscillatory) forms emerge. Thus, the Fisher–Widom line in the phase diagram may be interpreted as the boundary separating regions where

Kirkwood's pair correlation functions decay monotonically from those where damped oscillations dominate, thereby bridging phenomenological and microscopic descriptions of correlation decay in liquids.

2.7. Critical Fluctuations

A critical phenomenon refers to the divergence of a system's response to external fields in the disordered phase as the temperature approaches the critical temperature T_C . It describes the behavior of a system in the vicinity of a continuous phase transition. At the critical point, as mentioned earlier, the distinction between coexisting phases disappears, and the system begins to exhibit large-scale fluctuations of the order parameter, for example in composition. These fluctuations dominate the thermodynamic and structural properties of the material.[35]

Characteristic quantities, such as the correlation length ξ , diverge according to specific power laws. In a continuous phase transition, such divergences occur because the system becomes increasingly disordered for $T < T_C$. Here, T_C denotes the critical temperature.[14] A key feature of critical phenomena is the appearance of universal scaling laws and power-law divergences, which are characterized by so called critical exponents. Notably, quantities such as the correlation length ξ , the susceptibility χ , and the specific heat diverge according to power laws governed by these exponents.

A central quantity in the description of critical fluctuations is the two-point correlation function, defined as the following.[35]

$$g(\mathbf{r}) = \langle \delta\rho(0) \delta\rho(\mathbf{r}) \rangle, \quad (2.16)$$

And the density fluctuation is also a key parameter for critical fluctuations.

$$\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \langle \rho \rangle. \quad (2.17)$$

Close to the critical point, the spatial decay of correlations follows a generalized Ornstein-Zernike form.

$$g(r) \propto \frac{\exp(-\frac{r}{\xi})}{r^{d-2+\eta}}, \quad (2.18)$$

Where d is the dimensionality of the system, η is the anomalous dimension, and ξ is the correlation length.

The static structure factor $S(q)$, which is proportional to the scattering intensity $I(q)$, is given by the Fourier transform of the correlation function.

$$I(q) \propto |S(q)|^2 \propto \left| \int (g(|\mathbf{r}|) - 1) e^{i\mathbf{q}\cdot\mathbf{r}} d^3r \right|^2 \quad (2.19)$$

$$= \int g(|\mathbf{r}|) e^{i\mathbf{q}\cdot\mathbf{r}} d^3r \quad (2.20)$$

2. Theory

In the disordered phase far above T_c , the structure factor takes a Lorentzian form:

$$I(q) \propto \frac{1}{q^2 + \xi^{-2}}, \quad (2.21)$$

which reflects exponentially decaying density correlations in real space. This behavior becomes increasingly sharp as $T \rightarrow T_c$, with the width of the Lorentzian narrowing due to the divergence of ξ .

The divergence of key thermodynamic quantities near the critical point can be described using scaling relations. The correlation length behaves like this [38]

$$\xi \propto \xi_0 |\tau^2 + \delta^2|^{-\frac{\nu}{2}}, \quad (2.22)$$

And the susceptibility is defined as the following equation.

$$\chi \propto \chi_0 |\tau^2 + \delta^2|^{-\frac{\gamma}{2}}, \quad (2.23)$$

where

$$\tau = \frac{T - T_c}{T_c}, \quad \delta \propto x - x_c. \quad (2.24)$$

Here, τ is the reduced temperature, δ a compositional deviation from the critical concentration x_c , and ν, γ are universal critical exponents that depend only on the universality class of the system.

In soft matter systems undergoing demixing or microphase separation, the Ising model often serves as a reference for the expected critical behavior. Depending on the effective dimensionality of the system, the critical exponents can be taken from the exactly solvable 2D Ising model or from numerical simulations of the 3D case. For γ and ν the literature values are [38]

Exponent	2D Ising	3D Ising
Correlation length ν	0.63	1.00
Susceptibility γ	1.24	1.75

2.8. Ornstein-Zernike Theory

A theoretical framework for describing the structure of dense gases and fluids is provided by the Ornstein-Zernike equation. In the context of fluids, the Ornstein-Zernike theory characterizes density fluctuations near the critical point.[38] The theory was first introduced in 1914 by Ornstein and Zernike in their paper on the deviations of fluctuations at the critical point.[28]

To describe complex systems such as fluids, three correlation functions are typically required: the total correlation function $h(\mathbf{r}_1, \mathbf{r}_2)$, the direct correlation function $c(\mathbf{r}_1, \mathbf{r}_2)$, and the pair distribution function $g(\mathbf{r}_1, \mathbf{r}_2)$. The direct correlation function $c(\mathbf{r}_1, \mathbf{r}_2)$ is

2.8. Ornstein-Zernike Theory

short-ranged, acting primarily between nearest neighbors. In contrast, the total correlation function $h(\mathbf{r}_1, \mathbf{r}_2)$ captures both short- and long-range interactions, including contributions from more distant neighbors.[8]

The total correlation between two particles can be expressed as the sum of a direct correlation between them and an indirect correlation mediated by a third particle. This indirect contribution can be computed as

$$\int c(\mathbf{r}_1, \mathbf{r}_3) \rho^{(1)}(\mathbf{r}_3) c(\mathbf{r}_3, \mathbf{r}_2) d\mathbf{r}_3 \quad (2.25)$$

Through additional derivation steps, one arrives at an analytical expression for the total correlation function $h(\mathbf{r}_1, \mathbf{r}_2)$.

$$h(\mathbf{r}_1, \mathbf{r}_2) = c(\mathbf{r}_1, \mathbf{r}_2) + \rho \int h(\mathbf{r}_1, \mathbf{r}) c(\mathbf{r}, \mathbf{r}_2) d\mathbf{r} \quad (2.26)$$

This represents the most general form of the Ornstein–Zernike theory.[28]

A third important correlation function, which can be used to calculate the structure factor, is the pair distribution function $g(\mathbf{r}_1, \mathbf{r}_2)$. It is defined by the following equation

$$g(\mathbf{r}_1, \mathbf{r}_2) = h(\mathbf{r}_1, \mathbf{r}_2) + 1 \quad (2.27)$$

All three correlation functions are defined for any pair of particles within the system, but they can be naturally extended to include many-body correlations involving more than two particles.[8]

From the total correlation function $h(|\mathbf{r}|)$, the structure factor can be obtained via a Fourier transformation.

$$S(q) = 1 + \rho \int h(|\mathbf{r}|) \exp(i\mathbf{q}\mathbf{r}) d^3r \quad (2.28)$$

$$= 1 + \rho \int (g(|\mathbf{r}|) - 1) \exp(i\mathbf{q}\mathbf{r}) d^3r \quad (2.29)$$

Therefor, with Equation 2.20 the Intensity can be calculated from Equation 2.29

$$I(q) \propto |S_G|^2 \propto \left| \int (g(|\mathbf{r}|) - 1) \exp(i\mathbf{q}\mathbf{r}) d^3r \right|^2 \quad (2.30)$$

$$= \int g(|\mathbf{r}|) \exp(i\mathbf{q}\mathbf{r}) d^3r \quad (2.31)$$

It becomes evident that solving the Ornstein-Zernike equation generally requires an additional assumption, typically in the form of an approximation for the pair distribution function. This necessity arises because the Ornstein-Zernike relation, in its general form, involves two unknown functions, the total correlation function $h(\mathbf{r})$ and the direct correlation function $c(\mathbf{r})$. Without further constraints or closure relations, the equation remains underdetermined.

A commonly used approach is to approximate the pair distribution function $g(\mathbf{r})$, whose

2. Theory

correct form can, for example, be derived from the Ising model. A detailed derivation is provided in this paper [7]

$$g(|\mathbf{r}|) \sim \frac{\exp\left(-\frac{|\mathbf{r}|}{\xi}\right)}{|\mathbf{r}|^{\frac{(d-1)}{2}}} \quad (2.32)$$

$$= \frac{\exp\left(-\frac{|\mathbf{r}|}{\xi}\right)}{|\mathbf{r}|} \quad (2.33)$$

Here, ξ denotes the correlation length, and d represents the spatial dimensionality, which in our case is $d = 3$. Substituting this result into Equation 2.20 yields a specific form of the Ornstein-Zernike expression for the correlation length ξ . [45]

$$I(q) \propto \frac{1}{1 \pm \xi^2 q^2} \quad (2.34)$$

For a more detailed derivation, the complete calculations can be found in [7].

2.9. Double Lorentzian Model

For the double Lorentzian model, one can start from the pair correlation function derived within the Ornstein-Zernike framework see Equation 2.33. While the Ornstein-Zernike approach yields a single Lorentzian peak centered at $q_0 = 0$, the double Lorentzian model accounts for two symmetric or asymmetric Lorentzian contributions positioned at $q = \pm q_0$. [13] Physically, the Ornstein-Zernike correlation describes a monotonic decay of correlations, whereas the double Lorentzian form corresponds to oscillatory correlations in real space. [38][13].

This can be implemented by multiplying the Ornstein-Zernike pair correlation function with a modulation factor $\cos(q_0 r)$:

$$g(|\mathbf{r}|) = \frac{\exp\left(-\frac{|\mathbf{r}|}{\xi}\right)}{|\mathbf{r}|} \cos q_0 |\mathbf{r}| \quad (2.35)$$

where ξ is the correlation length. Inserting this expression into Equation 2.20 yields the following intensity profile for the double Lorentzian model.

$$I(q) \propto \frac{A_1}{(q - q_0)^2 + \xi^2} + \frac{A_2}{(q + q_0)^2 + \xi^2} \quad (2.36)$$

where A_1 and A_2 are the amplitudes of the two Lorentzian peaks.

2.10. Voigt Model

Voigt profiles arise when both homogeneous broadening, e.g. exponential decay of correlations (Lorentzian), and inhomogeneous broadening, e.g. instrumental resolution,

domain size distribution (Gaussian), are present. The Voigt profile is a convolution of a Lorentzian and a Gaussian [36]

$$V(q, q_0, \gamma, \sigma) = \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(q' - q_0)^2}{2\sigma^2}\right) \frac{A}{(q - q')^2 + \gamma^2} dq' \quad (2.37)$$

Where γ is the Lorentzian HWHM which is directly elated to correlation length ξ . σ is the standard deviation of Gaussian broadening which is related to the resolution and Acorrepsonds to the amplitude.

The double Voigt Model inculdest symmetric peaks at $\pm q_0$. To reach the $I(q)$ for this model one needs to calculate the pair distribution function for this sytem. The pair distribution function includes the two for the Lorentzian part and the Gaussain part. The Lorentzian part reflects an exponentially decaying correlation function while the Gaussian reflects static disorder.[36]

$$g_L(\mathbf{r}) \approx \exp(-\gamma\mathbf{r}) \quad \text{Lorentzian} \quad (2.38)$$

$$g_G(\mathbf{r}) \approx \exp(-\sigma^2\mathbf{r}^2) \quad \text{Gaussian} \quad (2.39)$$

$$\Rightarrow g(\mathbf{r}) \approx \exp(-\gamma\mathbf{r}) \exp(-\sigma^2\mathbf{r}^2) \cos(q_0\mathbf{r}) \quad (2.40)$$

While $q(\mathbf{r})$ is a damped oscillation with both exponential and Gaussian envelopes. Inserting this in Equation 2.20 one leads to the double Voigt profile.

$$I(q) = A [\text{Voigt}(q - q_0, \gamma, \sigma) + \text{Voigt}(q + q_0, \gamma, \sigma)] \quad (2.41)$$

2.11. Porod Model

The asymptotic behavior of small-angle scattering curves at high scattering vectors q was first systematically analyzed by Günther Porod in 1951 [39]. As mention in section 2.1, the intensity $I(q)$ is related to the Fourier transform of spatial correlations in the electron density $\rho(\vec{r})$. For two-phase systems with a sharp interface, the high- q behavior of the scattering curve follows the so-called Porod law. For general multiphase systems, where $\rho(\vec{r})$ is a piecewise constant function with sharp discontinuities at the interfaces between distinct domains, the scattering intensity can be written as Equation 2.20.[12] To obtain the Porod law one needs to determine the pais distribution function of the system.

The following dtermination is done after the work of Debey in [13]. For a system with two homogeneous phases A and B, the characteristic function of phase A is given y the following definition.

$$\chi_A(\mathbf{r}) = \begin{cases} 1 & \text{if } \mathbf{r} \in \text{Phase A,} \\ 0 & \text{otherwise.} \end{cases} \quad (2.42)$$

This gives an expression for the electron density:

$$\rho(\mathbf{r}) = \rho_A \chi_A(\mathbf{r}) + \rho_B (1 - \chi_A(\mathbf{r})) \quad (2.43)$$

2. Theory

The average is defined by the volume fraction of phase A, $\varphi_A = \langle \chi_A \rangle$:

$$\langle \rho \rangle = \rho_A \varphi_A + \rho_B (1 - \varphi_A), \quad (2.44)$$

Inserting this into Equation 2.17 gives an expression for the density fluctuations within the system:

$$\delta \rho(\mathbf{r}) = (\rho_A - \rho_B)(\chi_A(\mathbf{r}) - \varphi_A) \quad (2.45)$$

$$= \Delta \rho \cdot (\chi_A(\mathbf{r}) - \varphi_A), \quad (2.46)$$

where $\Delta \rho = \rho_A - \rho_B$.

For the autocorrelation function one inserts the results above into Equation 2.17:

$$\langle \delta \rho(0) \delta \rho(\mathbf{r}) \rangle = (\Delta \rho)^2 \langle (\chi_A(0) - \varphi_A)(\chi_A(\mathbf{r}) - \varphi_A) \rangle \quad (2.47)$$

$$= (\Delta \rho)^2 g(\mathbf{r}) \quad (2.48)$$

where $g(\mathbf{r})$ is the pair distribution function of the characteristic function.

For the intensity $I(q)$, inserting the pair distribution function into Equation 2.20 gives

$$I(\mathbf{r}) = (\Delta \rho)^2 \int g(\mathbf{r}) \exp i \vec{q} \cdot \mathbf{r} d^3 r \quad (2.49)$$

In the high- q limit, the integrand becomes highly oscillatory, and only regions with sharp variations in $\delta \rho(\mathbf{r})$, such as interfacial boundaries between phases, contribute significantly to the scattering signal. Therefore, by applying the Fourier transformation of the characteristic function, the intensity has in approximation the following form:

$$I(q) \propto C q^{-4} \propto q^{-4} \quad (2.50)$$

Porod showed in his paper from 1951 [39] that the prefactor C is well defined in the limit $q \rightarrow \infty$:

$$\lim_{q \rightarrow \infty} I(q) = \frac{2\pi(\Delta \rho)^2 S}{q^4}, \quad (2.51)$$

Equation 4.5 is also known as the general Porod law. [44]

As an additional measurement technique, attenuated total reflectance (ATR) spectroscopy was employed. This method provides complementary chemical information, allowing for verification of sample concentrations and related parameters. The setup and application of ATR will be described in detail in the following section.

2.12. Attenuated Total Reflectance (ATR)

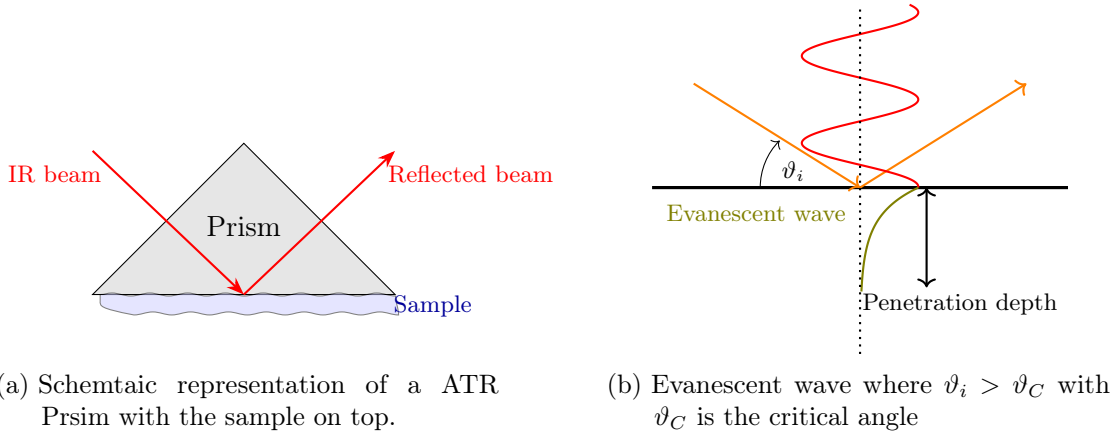


Figure 2.7.: Schematic illustration of the working principle of attenuated total reflectance (ATR). Infrared radiation undergoes total internal reflection at the interface between the ATR crystal and the sample. An evanescent wave penetrates into the sample, where absorption occurs depending on the vibrational modes of the molecules.

2.12. Attenuated Total Reflectance (ATR)

Attenuated Total Reflectance (ATR) is a specific type of Infrared spectroscopy and based on the optical principle of total internal reflection. The method was first introduced by Fahrenfort in 1961 in his paper on attenuated total reflection.[15] ATR is commonly used to obtain infrared (IR) spectra of solids and thin films.[11]

For total internal reflection to occur, the angle of incidence ϑ_i must satisfy the following condition

$$\sin \vartheta_i > \frac{n_2}{n_1} \quad (2.52)$$

where n_1 and n_2 are the refractive indices of the optically denser and rarer media, respectively.

Under this condition, complete reflection occurs within the denser optical medium because the angle of refraction ϑ_{sc} becomes imaginary. This phenomenon gives rise to an evanescent wave that penetrates a short distance beyond the interface into the rarer medium. The evanescent wave has the same frequency as the totally reflected radiation and interacts with the sample at the interface, causing a measurable attenuation of the reflected beam.[11]

3. Methods and Materials

This chapter provides an overview of the materials and experimental methods used in this work. It begins with a description of the small-angle X-ray scattering (SAXS) setup, which served as the primary technique to investigate the structural properties of the samples across different length scales. Complementary chemical information was obtained using attenuated total reflectance (ATR) spectroscopy, which enabled the characterization of functional groups and the detection of changes in molecular interactions. In addition, the chemical materials employed in this study are listed together with their relevant specifications. Finally, the procedures for sample preparation are described, including the calculation of the required concentrations and the preparation steps for the HFIP-water mixtures and their modifications with additives such as acids or antagonistic salts.

3.1. Small Angle X-ray scattering

All measurements were performed using the Bruker AXS Nanostar small-angle X-ray scattering (SAXS) system. Figure 3.1 provides an overview of the experimental setup, showing (i) the general laboratory setup, (ii) the X-ray tube with the collimation system, (iii) the vacuum chamber, and (iv) the germanium scatter-free pinholes of the two-pinhole collimation system.

The X-ray source used was the Incoatec ixtube-Cu-50 microfocus tube with a copper (Cu) target produced in 2017 (Type: HB025R1). It generates $\text{CuK}\alpha$ radiation with a wavelength of $\lambda = 1.54 \text{ \AA}$, corresponding to a photon energy of $E = 8.04 \text{ keV}$. A 0.1 mm thick beryllium foil serves as both a spectral filter, providing a clean X-ray beam, and as a vacuum barrier for the tube, while transmitting the beam with minimal absorption. The X-ray tube was operated at an acceleration voltage of 50 kV and a current of 1 mA. In the standby mode the acceleration voltage is reduced to 20 kV and the current to 0.2 mA. [23]

In combination of the source is a beam shaping and monochromatization setup. X-ray beam collimation and monochromatization were achieved using a Montel optics module provided by Incoatec GmbH (Geesthacht, Germany). The Montel system consists of two multilayer-coated mirrors arranged orthogonally in an L-shape configuration, allowing for two-dimensional beam shaping through total external reflections. The mirrors are coated with W/C multilayers, which collect X-rays within following Bragg's law in a narrow angular range (FWHM = 1 mrad for Cu radiation), reflect them toward the sample with high efficiency (up to 80%), and provide spectral purification by suppressing the K_β component to below 0.5%. Because the beam undergoes two reflections, the monochromatization effect is effectively squared. Montel optics are particularly suited for

3. Methods and Materials

microfocus X-ray sources with small anode spot sizes ($< 100 \mu\text{m}$), enabling symmetrical beam profiles with low divergence and high brilliance. [19] The Incoatec ixtube-Cu-50 has a spot size of $50 \mu\text{m} \times 50 \mu\text{m}$. [23] For SAXS measurements, the distance between the



Figure 3.1.: Components of the Bruker AXS Nanostar Small Angle X-ray Scattering setup. (i) General view of the instrument. (ii) X-ray tube and beam collimation stage. (iii) Sample vacuum chamber inside the protective housing. (iv) Scatter-free pinholes (diameter $300 \mu\text{m}$, Ge) applied for beam shaping and reduction of parasitic scattering.

sample and the detector was approximately 114 mm, while for WAXS measurements it was about 28 mm. The exact distances were calibrated using the program Datasqueeze, and the corresponding q -ranges are listed in Appendix A.3.

The instrument is equipped with a VÅNTEC 2000 area detector, shown on the right-hand side of Figure 3.1(i). This gas-filled detector (2 atm xenon-based proprietary gas mixture) employs microgap technology. It consists of 2048×2048 pixels with a pixel size of $68 \times 68 \mu\text{m}^2$. [24]

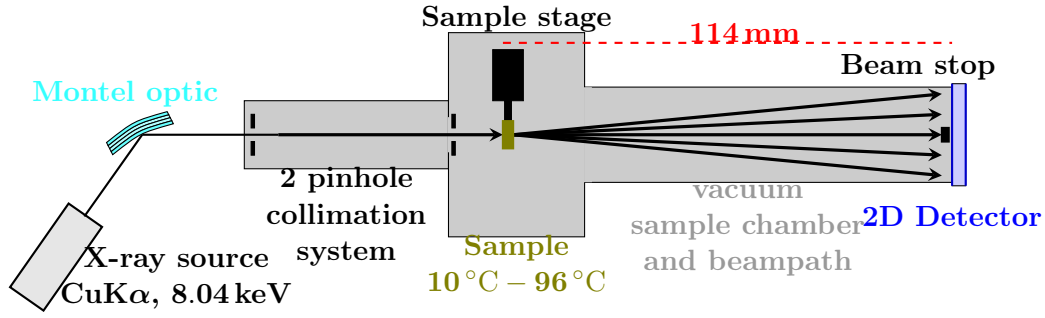


Figure 3.2.: Schematic setup of the Bruker AXS Nanostar SAXS instrument. The X-ray beam ($\text{CuK}\alpha$, 8.04 keV) is focused by a Montel optic and collimated by a two-pinhole system before reaching the sample stage. The sample environment allows temperature control between 10°C and 96°C. Scattered X-rays are recorded by a 2D detector placed at a distance of 114 mm behind the sample (for SAXS), with a beam stop blocking the transmitted beam.



Figure 3.3.: Temperature control unit coupled to the Bruker AXS Nanostar SAXS setup. (i) Fisher Scientific Cooling device with Bruker control panel. (ii) Integration of the cooling unit with the SAXS instrument for performing temperature-dependent measurements.

Temperature-dependent measurements were performed using the Bruker Nanostar Heating Stage H with the TCPU H controller, combined with a Heated Immersion Circulator R20F and an Isotemp 6200 unit from Fisher Scientific, Inc. With this setup, the temperature could be varied between 10°C and 96°C. Figure 3.3 shows the cooling and heating setup: the Isotemp 6200 is placed on top of the immersion circulator, which is directly connected to the heating stage. The cooling water has a temperature of 5°C. For the Druchfluss the high pressure is around 20.4 and for low pressure 10. The heating element is controlled via a separate unit linked to the computer system. A schematic overview of the entire SAXS setup is shown in Figure 3.2, where the beam path is indicated by black arrows. The sample stage, located inside the vacuum chamber, can be moved with a step size of 10 μm and is controlled by the instrument software.[18]

3. Methods and Materials

Figure 3.4 illustrates the sample holders used during the measurements. Figure 3.4(ii) shows the holder for room-temperature experiments, accommodating up to ten capillaries simultaneously. In contrast, Figure 3.4(i) displays the holder positioned in the vacuum chamber on top of the sample stage. For temperature-controlled experiments, the holder shown in Figure 3.4(iii) and Figure 3.4(iv) was used, which can accommodate up to three capillaries per measurement cycle. All measurements were conducted under vacuum conditions at approximately 10^{-1} mbar.

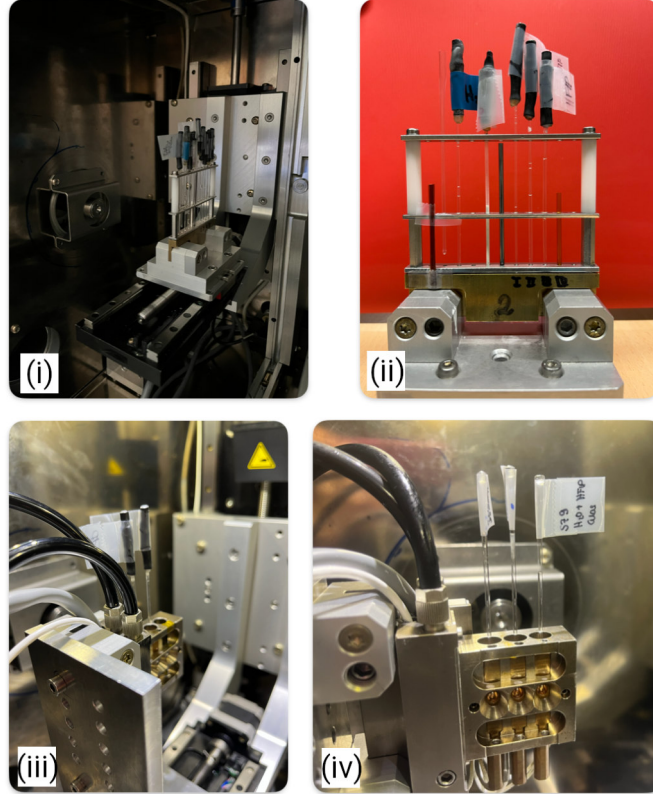
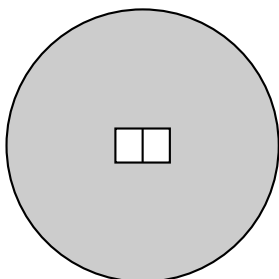


Figure 3.4.: Sample holders used in the Bruker AXS Nanostar SAXS setup. (i) Sample holder stage for room temperature measurements inside the vacuum chamber. (ii) Sample holder stage for capillaries outside the chamber. (iii) Temperature controlled sample stage in the vacuum chamber. (iv) heating block with copper sample holder for 3 capillaries.

3.2. Attenuated Total Reflectance

The Measurements for the Attenuated Total Reflectance Spectra was performed by the Bruker Tensor 27 ATR. The Bruker Tensor 27 is an ATR spectrometer equipped with a



ATR Measurement plate (Top View)

diamond ATR crystal. On the left side of the device, the ATR measurement plate is located, while the white square in the center represents the diamond crystal. For measurements, a small amount of the sample is placed directly on the crystal. To prevent damage to the diamond, certain sample properties such as the pH value must be known in advance. The crystal can withstand pH values in the range of 0 to 14. The instrument features a spectral resolution of 0.4 cm^{-1} and a wavenumber accuracy of 0.01 cm^{-1} .

It is equipped with a built-in HeNe laser (class 2) with an output power of $P_{\text{out}} = 1\text{ mW}$, a wavelength of $\lambda = 633\text{ nm}$, and a divergence angle of $1.77\text{ mrad} \pm 5\%$. The accessible spectral range of the Bruker Tensor 27 extends from 8000 to 340 cm^{-1} . [6]

Prior to measuring a sample spectrum, background spectra were collected. One background measurement was recorded by exposing the ATR crystal to the ambient environment, while another was taken using pure water as a reference. All spectra were recorded using Bruker's OPUS software. The data were saved in `.txt` format, containing absorbance values and corresponding wavenumbers. Measurement parameters such as number of scans, acquisition time, and spectral range are user defined within the software interface. After each measurement, the ATR crystal was thoroughly cleaned with acetone and lint-free tissues. To ensure the absence of contamination, a background spectrum was taken after cleaning and visually inspected for residual peaks.

The subsequent data analysis was performed using Python, where the exported `.txt` files were processed and the spectra plotted.

3.3. Chemical Components

The properties and interactions of the individual components fundamentally determine the behavior of complex liquid systems, particularly in relation to solubility, miscibility, and phase separation. Key molecular features such as polarity, hydrogen bond donor and acceptor capacity, acidity or basicity, and ionic character influence both local structure and macroscopic phase behavior. This section provides an overview of the chemical substances used in this study, highlighting their physicochemical characteristics and their specific roles within the solvent mixture and its associated phase behavior. The important parameter can be found in Table A.2. The chemical concepts discussed in this section are based on standard chemistry textbooks such as [3], [2], and [37]. In addition, selected results from recent studies [10],[47] are taken into account.

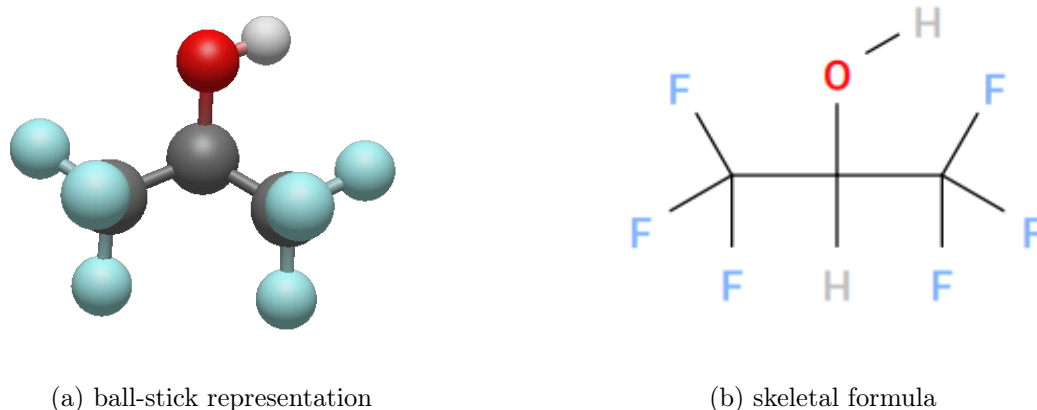


Figure 3.5.: Molecular representation of Hexafluoroisopropanol

3.3.1. Hexafluoroisopropanol (HFIP)

Hexafluoroisopropanol (HFIP) is a fluorinated alcohol with physicochemical properties that make it a widely used solvent in organic and materials chemistry and called 'miracle solvent'.^[25] Due to its high miscibility with both water and alcohols, thermal stability, and relatively low boiling point (59 °C), HFIP is easy to recover, which makes it especially useful in laboratory-scale applications.

HFIP exhibits significantly enhanced acidity ($pK_a = 9.3$) compared to isopropanol ($pK_a = 17.1$) owing to the electron withdrawing trifluoromethyl groups, while remaining extremely low in nucleophilicity. ^[10] It is also characterized by a strong hydrogen bond donor ability, which leads to the formation of stable solvation structures. DFT calculations have shown that HFIP can form stable trimers through hydrogen bonding, further amplifying its donor properties.

This ability enables HFIP to activate a broad range of functional groups, including carbonyls and alcohols via noncovalent interactions, facilitating various transformations. ^[10]

HFIP also displays high electrochemical stability and a wide electrochemical window, making it an attractive medium under oxidative conditions and in electrochemical applications. Its low basicity and relatively high dielectric constant ($\epsilon = 15.7$) support the stabilization of cationic intermediates, such as allyl or benzyl cations.

In aqueous HFIP mixtures, a triphasic nanostructure has been reported, consisting of distinct fluorophilic, aqueous and hydrophobic organic microphases. This microscopic heterogeneity influences the aggregation and self-assembly behavior of solutes.^[10]

Structurally, HFIP consists of a central hydroxyl group flanked by two trifluoromethyl ($-\text{CF}_3$) groups. From a molecular interaction standpoint, HFIP acts as a hydrogen bond donor but a poor acceptor, due to the low basicity of its oxygen lone pair and steric hindrance from the CF_3 groups. Consequently, HFIP exhibits strong interactions with Lewis bases, like for example water and amides, while repelling other donors or nonpolar

molecules.

The exact numbers can be found in A.2.

HFIP also has a high cohesive energy density due to its bipolar and hydrogen bonding contributions.

These features make HFIP an anomalous solvent, especially when mixed with water or ionic species. While it is fully miscible with water at standard conditions, mixtures exhibit complex microheterogeneous structures and may undergo temperature-driven phase separation, depending on the presence of cosolutes, like salts or acids.

From a thermodynamic perspective, HFIP-water mixtures can exhibit non-ideal mixing behavior, manifesting as Upper or Lower Critical Solution Temperature (UCST/LCST) phenomena when perturbed.

HFIP as an amphiphilic compound

As mentioned earlier, amphiphilic compounds possess two distinct parts: one polar and one apolar. This amphiphilic nature is also one of the most characteristic properties of HFIP. Figure 3.6a illustrates the molecular structure of Hexafluoroisopropanol, where the apolar moiety is highlighted in orange and the polar hydroxyl group is shown in green.

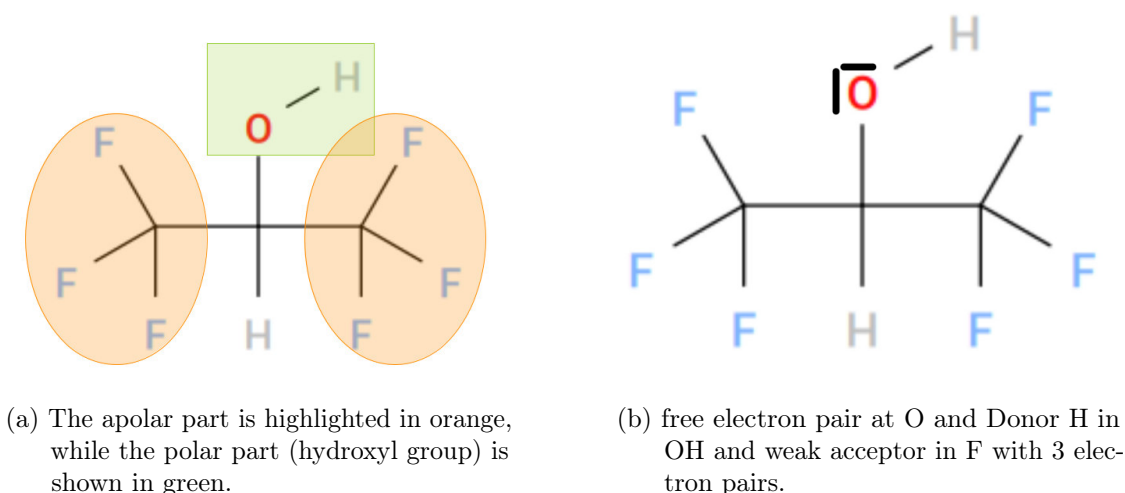


Figure 3.6.: Skeletal formula of HFIP as an amphiphilic compound

The hydrogen atom, not explicitly indicated in the skeletal formula, forms a covalent bond with carbon but is only weakly polarized. In this context, the C–H bond is considered relatively unreactive, especially in comparison to the strongly polar hydroxyl group. As the HFIP concentration increases, HFIP molecules preferentially interact with and solvate the hydrophobic regions of the solute. This selective solvation leads to the formation of HFIP-enriched domains. These domains increasingly exclude water, ultimately inducing phase separation in the HFIP-water system. [46]

3.3.2. Fluorinated carboxylic Acid

Pentafluoropropionic acid ($\text{C}_3\text{HF}_5\text{O}_2$) is a short-chain perfluorinated carboxylic acid characterized by the strong electron-withdrawing effect of its five fluorine substituents. This leads to a pronounced acidity with a pK_a which is significantly lower than that of non-fluorinated carboxylic acids. The corresponding values can be found in Table A.2. Owing to its amphiphilic nature, $\text{C}_3\text{HF}_5\text{O}_2$ combines a highly hydrophobic perfluoroalkyl tail with a polar carboxylic headgroup. In aqueous solution, this duality results in strong tendencies toward self-assembly and micellization at interfaces. Compared to longer perfluorocarboxylic acids, $\text{C}_3\text{HF}_5\text{O}_2$ is more soluble in water but retains the typical features of fluorinated surfactants, including high chemical stability, low polarizability and strong perturbation of the hydrogen-bonding network of water.

In ternary mixtures of HFIP and water, the distribution of $\text{C}_3\text{HF}_5\text{O}_2$ is governed by its amphiphilic character. The carboxylic acid group shows strong affinity for the aqueous phase, where it can engage in hydrogen bonding and proton transfer, whereas the perfluorinated tail is preferentially solvated in the HFIP-rich phase due to the compatibility of fluorinated environments. As a result, $\text{C}_3\text{HF}_5\text{O}_2$ tends to accumulate at the interface between HFIP-rich and water-rich domains, effectively acting as a surfactant. Depending on concentration, this can either stabilize mixed phases or drive phase separation. In equilibrium, the protonated acid predominantly partitions into the HFIP-rich phase through hydrophobic and fluorophilic interactions, while its deprotonated form is more soluble in the aqueous phase.

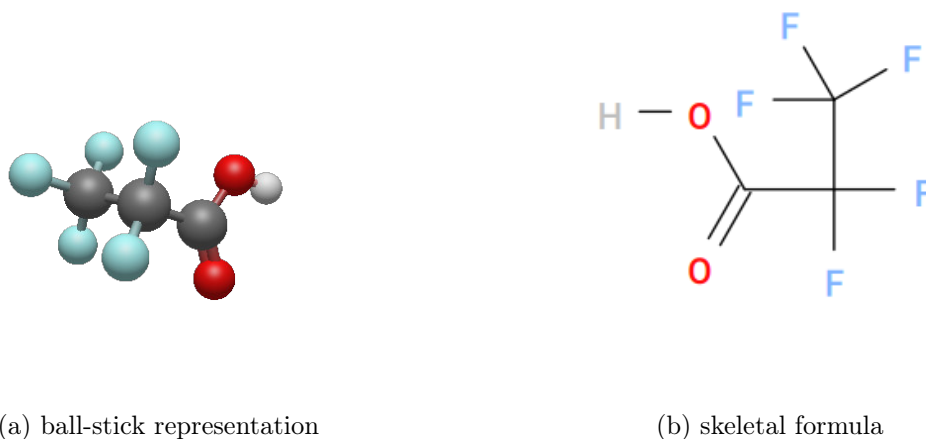


Figure 3.7.: Molecular representation of Pentafluoropropionic acid $\text{C}_3\text{HF}_5\text{O}_2$.

Perfluorohexanoic acid $\text{C}_6\text{HF}_{11}\text{O}_2$ is a medium long chain perfluorinated carboxylic acid belonging to the class of PFAS. Its perfluorohexyl chain confers a pronounced hydrophobic and lipophobic character, while the strongly electron-withdrawing fluorine substituents increase the acidity of the carboxyl group. Compared to short-chain analogues such as pentafluoropropionic acid, $\text{C}_6\text{HF}_{11}\text{O}_2$ exhibits reduced water solubility and a stronger

3.3. Chemical Components

tendency to adsorb at hydrophobic or fluorinated interfaces. This amphiphilic nature allows $\text{C}_6\text{HF}_{11}\text{O}_2$ to act as a surfactant, promoting aggregate formation. Figure 2.4a provides an overview of all potential formation pathways.

In ternary HFIP-water mixtures, $\text{C}_6\text{HF}_{11}\text{O}_2$ partitions according to its dual chemical character. The carboxylic headgroup interacts favorably with the aqueous phase via hydrogen bonding and ionization, while the extended perfluoroalkyl chain is more compatible with the HFIP-rich phase. Consequently, $\text{C}_6\text{HF}_{11}\text{O}_2$ tends to accumulate at the HFIP-water interface, enriching the phase boundary and altering the miscibility of the two solvents. At low concentrations this can stabilize microheterogeneous structures, while at higher concentrations $\text{C}_6\text{HF}_{11}\text{O}_2$ can promote phase separation by segregating into the HFIP-rich domains with its tail, leaving the polar headgroup in contact with the aqueous phase. In equilibrium, the protonated species favors the HFIP-rich phase, whereas the deprotonated anion exhibits higher solubility in the water-rich phase.

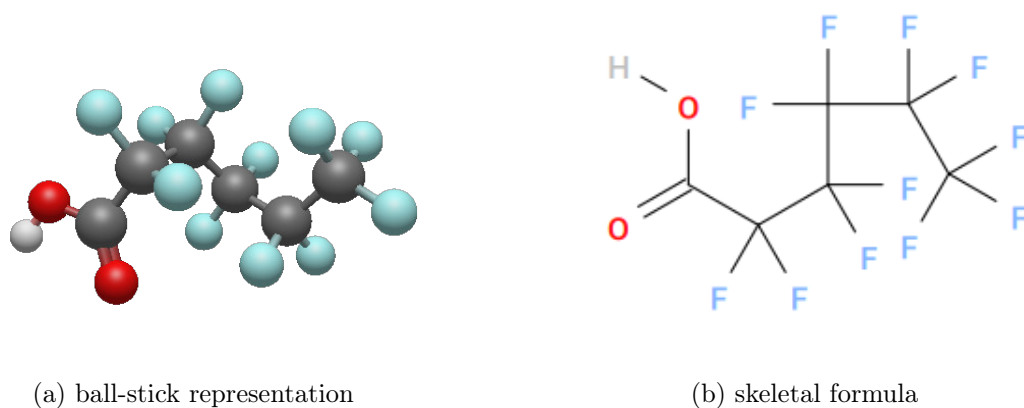


Figure 3.8.: Molecular representation of Perfluorohexanoic acid $\text{C}_6\text{HF}_{11}\text{O}_2$.

3.3.3. Sodium Hydroxide (NaOH)

Sodium hydroxide (NaOH) is a strong, monoprotic inorganic base that dissociates completely in aqueous solution to form sodium (Na^+) and hydroxide (OH^-) ions. Its high basicity and strong nucleophilicity make it a widely used reagent in both laboratory and industrial contexts. In aqueous environments, NaOH readily raises the pH of solutions and serves as a key tool for neutralization, saponification, and deprotonation reactions. Due to its complete dissociation in water, NaOH provides a highly alkaline environment (typical $\text{pH} > 13$ at moderate concentrations), which can drastically alter the protonation states of solutes. For example, weak acids such as carboxylic acids or alcohols become deprotonated in the presence of NaOH, forming their corresponding carboxylate or alkoxide ions. This property is exploited in a wide range of chemical processes, including hydrolysis, base-catalyzed condensation, and phase transfer reactions.

In mixtures with fluorinated alcohols like HFIP, the presence of NaOH leads to partial or

3. Methods and Materials



Figure 3.9.: Molecular representation of Sodium Hydroxide NaOH.

complete deprotonation of HFIP and other weak acids, affecting the hydrogen-bonding network and overall solvation structure. This can impact both the chemical reactivity and the supramolecular organization of the system. Additionally, in systems containing self-assembling amphiphiles or acids, NaOH can induce structural changes by converting neutral species into charged forms, thereby modifying intermolecular interactions, solubility, and aggregation behavior.

Solid NaOH is highly hygroscopic and must be handled under dry conditions to avoid absorption of water and carbon dioxide from the atmosphere, which would otherwise lead to the formation of sodium carbonate and a decrease in base strength. For precise solution preparation, NaOH is usually dissolved in deionized water and standardized via titration.

3.3.4. Tetraphenylphosphonium Chlorid (TPhP^+Cl^-)

Tetraphenylphosphonium chloride (TPhP^+Cl^-) is a quaternary phosphonium salt composed of a large, lipophilic tetraphenylphosphonium ($(\text{C}_6\text{H}_5)_4\text{P}^+$) cation and a chloride (Cl^-) counterion. The phosphonium core includes four phenyl substituents, which contribute to its low charge density, high hydrophobicity, and poor solvation in aqueous media. The tetraphenylphosphonium cation is electrostatically stable and does not participate in proton transfer or hydrogen bonding. It is considered neither acidic nor basic and remains largely chemically inert in solution. Due to its size and aromatic structure, the cation can, however, engage in ion pairing with large anionic species in nonpolar solvents.

In the context of HFIP-water mixtures, the solubility behavior of TPhP^+Cl^- is highly asymmetric. The chloride anion Cl^- is strongly hydrated and preferentially partitions into the water phase, where it can establish stabilizing hydrogen-bonding interactions with water molecules. In contrast, the tetraphenylphosphonium cation $(\text{C}_6\text{H}_5)_4\text{P}^+$ is poorly solvated in water due to its hydrophobic aromatic substituents and low charge density. Instead, it shows a much higher affinity for the HFIP-rich phase, where fluorophilic and hydrophobic interactions provide a more favorable solvation environment. This

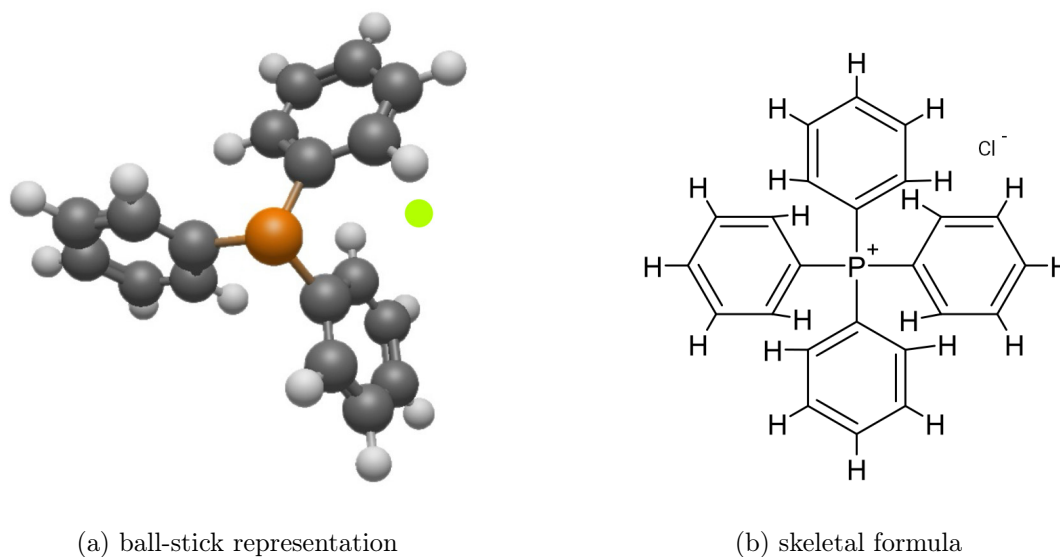


Figure 3.10.: Molecular representation of Tetraphenylphosphonium Chloride TPhP^+Cl^- .

partitioning tendency effectively drives the cation and anion into different local solvation environments, thereby creating microheterogeneities in the binary solvent system. In soft matter, TPhP^+Cl^- is frequently used as a counterion to tune ionic strength or to replace smaller cations (such as Na^+) in order to study ion-specific effects or aggregation behavior. In systems containing fluorinated alcohols such as HFIP, the phosphonium cation can influence phase behavior indirectly by affecting the electrostatic environment.

3.3.5. Sodium tetraphenylborate (NaBPh_4)

Sodium tetraphenylborate NaBPh_4 was employed in this study as part of a complementary ion pair with tetraphenylphosphonium chloride PPh_4Cl , commonly referred to as a mirror salt system. The use of this compound allows for a direct comparison between structurally analogous cations and anions, providing deeper insight into ion-specific effects in the investigated solvent systems. Sodium tetraphenylborate (NaBPh_4) is composed of a small sodium cation (Na^+) and the bulky tetraphenylborate anion ($\text{B}(\text{C}_6\text{H}_5)_4^-$). In the anion, four phenyl groups are arranged around the central boron atom in a roughly tetrahedral geometry, which disperses the negative charge over the aromatic rings. This delocalization renders BPh_4^- only weakly coordinating and prevents it from engaging in strong interactions with either cations or solvent molecules.

Because of its size and hydrophobic character, tetraphenylborate dissolves poorly in water but is compatible with many organic and especially fluorinated solvents. It does not take part in hydrogen bonding and is chemically inert under most conditions. These features make NaBPh_4 a valuable probe in solution chemistry, for instance when studying ion pairing, solvent organization, or electrostatic interactions.

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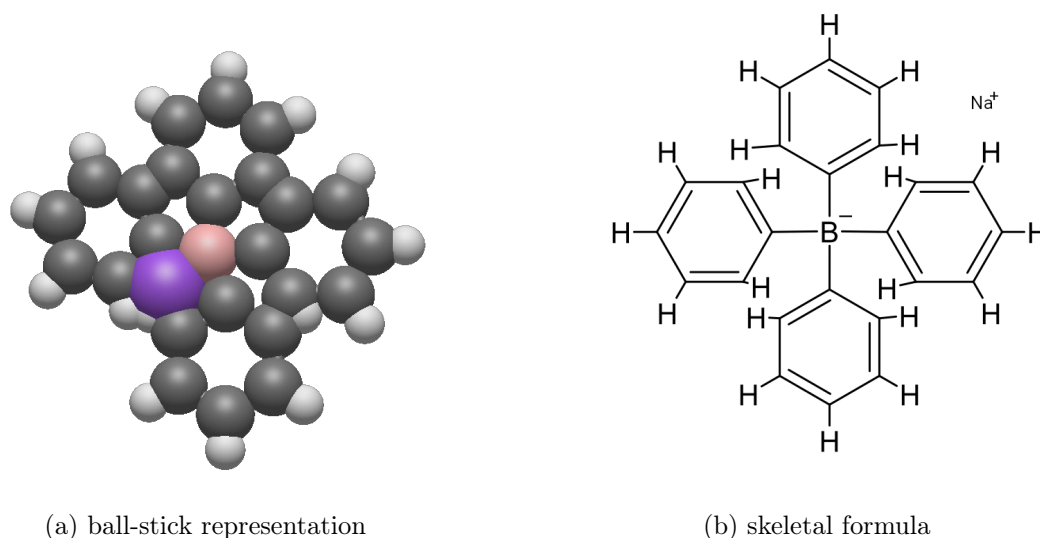


Figure 3.11.: Molecular representation of Sodium Tetraphenylborate NaBPh_4 .

When added to mixed solvents such as Hexafluoroisopropanol (HFIP) and water, NaBPh_4 can alter the structural balance of the system without undergoing direct acid–base chemistry. Interestingly, experiments have shown that its addition can raise the apparent pH of HFIP–water mixtures, even though the salt itself is neither acidic nor basic. This effect is likely related to subtle modifications of the hydrogen-bonding network and to a decrease in effective proton activity caused by weak ion pairing or rearrangement of the solvent structure.

3.4. Sample preparation

The sample preparation includes both the preparation of the specimens and the calculation of the appropriate amounts of the chemicals. For the production of the samples, the concentrations and needed volumes of the substances were calculated at first. At the beginning, the mole fractions were defined, and from these the required volumes were calculated.

All components were weighed using a precision balance.

The calculated amounts of substances were then mixed in a standard glass vessel in the chemistry laboratory.

For accurate measurement, syringes with a 0.01 mL scale were used.

The experiments were performed with samples filled into borosilicate glass capillaries (XRD capillaries from Hilgenberg) with an outer diameter of 1.5 mm and a wall thickness of approximately 10 μm .

The choice of capillary geometry was based on calculated absorption lengths for the

3.4. Sample preparation

relevant sample compositions under Cu K α radiation ($\lambda = 1.54 \text{ \AA}$).

$$I = I_0 \exp\left(\frac{-x}{\lambda}\right) \quad \text{with} \quad \lambda = \frac{1}{\mu} \quad (3.1)$$

Where μ is the linear attenuation coefficient, x the thickness and λ the wavelength. [22] For pure hexafluoroisopropanol, the linear attenuation coefficient was estimated to be approximately $\mu = 2.1 \text{ mm}^{-1}$, resulting in an absorption length $\lambda \approx 0.48 \text{ mm}$. [34]

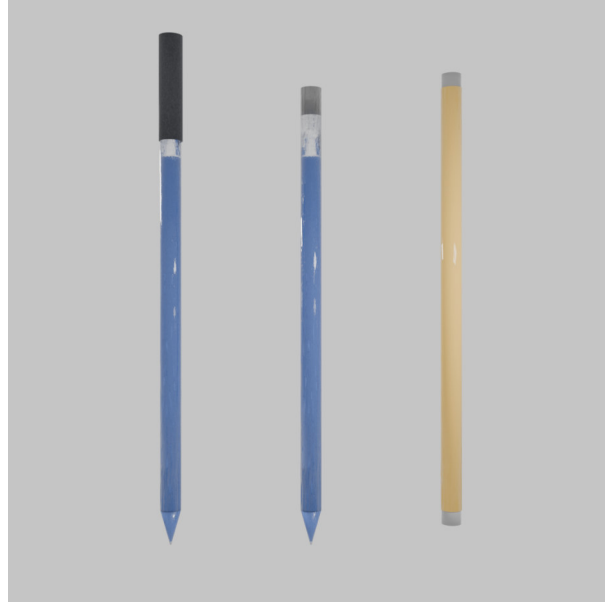


Figure 3.12.: Schematic overview of three types of prepared capillaries for the measurements. Left: Glass capillary sealed with black heat-shrink. Middle: Glass capillary sealed with grey epoxy adhesive. Right: Kapton (polyamid) foil capillary for X-ray transparency. All capillaries are filled with blue sample material for illustration. This image is performed via Blender

To balance between sufficient transmission and scattering volume, capillary diameter 1.5 mm was selected. This configuration allowed sufficient beam penetration while maintaining adequate path length for measurable scattering intensity.

Since the incident X-ray beam is significantly broader than the diameter of the capillary, photons traverse the sample under slightly different path lengths depending on their position within the beam profile. Photons entering near the edge of the capillary pass through a shorter effective distance compared to those entering along the central axis. This effect leads to a position-dependent attenuation of the beam and is illustrated schematically in Figure 3.13. To further minimize background scattering, a series of preliminary tests were performed using 0.6mm Kapton capillaries were used. However, no significant improvement in the signal-to-noise ratio was observed, and this modification was therefore omitted in the final setup.

3. Methods and Materials

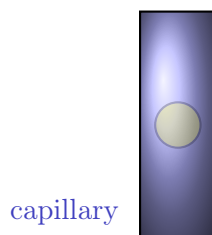


Figure 3.13.: Sketch of the X-ray beam (yellow circle) entering the capillary

Regarding sample sealing, several methods were explored. Initially, a combination of paraffin wax and heat-shrink tubing was employed to close the open ends of the capillaries. Although this method provided basic mechanical sealing, it occasionally resulted in microscopic leaks and solvent evaporation, which is particularly problematic for volatile components like HFIP. Subsequently, this method was replaced by a more robust closure using UV-curing adhesive (UHU LED-Light Booster). The adhesive was applied directly to the capillary opening and cured with UV light for approximately 15 s, creating a chemically resistant, airtight seal.

Samples were stored upright at room temperature. The following table is the sample list of all produced mixtures. It contains all the components, weight percentages, mole fractions, concentrations and pH values.

3.4. Sample preparation

Sample	Components	Mass %	Molbrüche x	concentration molL ⁻¹	pH
SZ0	HFIP-H ₂ O	HFIP: 43.96 H ₂ O: 56.04	$x_{HFIP} = 0.0776$ $x_{H_2O} = 0.9224$	$c_{HFIP} = 3.1$ $c_{H_2O} = 36.99$	5
SZ1	HFIP-H ₂ O-C ₃ HF ₅ O ₂	HFIP: 39.23 H ₂ O: 55.29 C ₃ HF ₅ O ₂ : 5.47	$x_{HFIP} = 0.077$ $x_{H_2O} = 0.92$ $x_{C_3HF_5O_2} = 0.001$	$c_{HFIP} = 3.1$ $c_{H_2O} = 36.48$ $c_{Acid} = 0.063$	1
SZ2	HFIP-H ₂ O-C ₃ HF ₅ O ₂	HFIP: 24.94 H ₂ O: 62.87 C ₃ HF ₅ O ₂ : 12.18	$x_{HFIP} = 0.039$ $x_{H_2O} = 0.94$ $x_{C_3HF_5O_2} = 0.021$	$c_{HFIP} = 1.68$ $c_{H_2O} = 40.93$ $c_{Acid} = 0.67$	1
SZ3	HFIP-H ₂ O-C ₃ HF ₅ O ₂ -NaOH	HFIP: 25.67 H ₂ O: 72.23 C ₃ HF ₅ O ₂ : 0.5 NaOH: 1.60	$x_{HFIP} = 0.02$ $x_{H_2O} = 0.96$ $x_{C_3HF_5O_2} = 0.01$ $x_{NaOH} = 0.01$	$c_{HFIP} = 0.86$ $c_{H_2O} = 46.1$ $c_{Acid} = 0.45$ $c_{NaOH} = 0.45$	10
SZ4	HFIP-H ₂ O-C ₃ HF ₅ O ₂ -NaOH	HFIP: 19.93 H ₂ O: 66.98 C ₃ HF ₅ O ₂ : 11.03 NaOH: 2.06	$x_{HFIP} = 0.03$ $x_{H_2O} = 0.94$ $x_{C_3HF_5O_2} = 0.017$ $x_{NaOH} = 0.013$	$c_{HFIP} = 1.885$ $c_{H_2O} = 67.09$ $c_{Acid} = 0.743$ $c_{NaOH} = 0.878$	0
SZ5	HFIP-H ₂ O-C ₃ HF ₅ O ₂	HFIP: 41.79 H ₂ O: 53.09 C ₃ HF ₅ O ₂ : 5.12	$x_{HFIP} = 0.07705$ $x_{H_2O} = 0.9129$ $x_{C_3HF_5O_2} = 0.00997$	$c_{HFIP} = 2.99$ $c_{H_2O} = 35.432$ $c_{Acid} = 0.387$	1
SZ6	HFIP-H ₂ O-C ₃ HF ₅ O ₂ -NaOH	HFIP: 41.48 H ₂ O: 52.04 C ₃ HF ₅ O ₂ : 5.25 NaOH: 1.24	$x_{HFIP} = 0.07719$ $x_{H_2O} = 0.9031$ $x_{C_3HF_5O_2} = 0.01$ $x_{NaOH} = 0.00967$	$c_{HFIP} = 2.96$ $c_{H_2O} = 34.728$ $c_{Acid} = 0.3849$ $c_{NaOH} = 0.3718$	0
SZ7	HFIP-H ₂ O	HFIP: 44.03 H ₂ O: 55.96	$x_{HFIP} = 0.0778$ $x_{H_2O} = 0.9222$	$c_{HFIP} = 3.14$ $c_{H_2O} = 37.18$	5
SZ8	HFIP-H ₂ O	HFIP: 39.33 H ₂ O: 60.67	$x_{HFIP} = 0.065$ $x_{H_2O} = 0.935$	$c_{HFIP} = 2.745$ $c_{H_2O} = 39.47$	5
SZ9	HFIP-H ₂ O	HFIP: 35.18 H ₂ O: 64.82	$x_{HFIP} = 0.055$ $x_{H_2O} = 0.945$	$c_{HFIP} = 2.41$ $c_{H_2O} = 41.42$	6

3. Methods and Materials

Sample	Components	Mass %	Molbrüche x	concentration molL ⁻¹	pH
SZ10	HFIP-H ₂ O	HFIP: 45.44 H ₂ O: 54.56	$x_{HFIP} = 0.082$ $x_{H_2O} = 0.918$	$c_{HFIP} = 3.26$ $c_{H_2O} = 36.47$	5
SZ11	HFIP-H ₂ O	HFIP: 47.67 H ₂ O: 52.33	$x_{HFIP} = 0.089$ $x_{H_2O} = 0.911$	$c_{HFIP} = 3.45$ $c_{H_2O} = 35.33$	5
SZ12	HFIP-H ₂ O-C ₂₄ H ₂₀ PCl	HFIP: 43.29 H ₂ O: 55.10 TPHP+Cl ⁻ : 1.62	$x_{HFIP} = 0.0777$ $x_{H_2O} = 0.9223$ $x_{TPHP+Cl^-} = 0.0013$	$c_{HFIP} = 3.13$ $c_{H_2O} = 37.19$ $c_{TPHP+Cl^-} = 0.050$	4
SZ13	HFIP-H ₂ O-C ₂₄ H ₂₀ PCl	HFIP: 43.29 H ₂ O: 55.10 TPHP+Cl ⁻ : 1.62	$x_{HFIP} = 0.0777$ $x_{H_2O} = 0.9223$ $x_{TPHP+Cl^-} = 0.0013$	$c_{HFIP} = 3.13$ $c_{H_2O} = 37.19$ $c_{TPHP+Cl^-} = 0.050$	4
SZ14	HFIP-H ₂ O-C ₂₄ H ₂₀ PCl	HFIP: 42.15 H ₂ O: 53.79 TPHP+Cl ⁻ : 5.90	$x_{HFIP} = 0.0772$ $x_{H_2O} = 0.9181$ $x_{TPHP+Cl^-} = 0.00485$	$c_{HFIP} = 3.13$ $c_{H_2O} = 37.2$ $c_{TPHP+Cl^-} = 0.196$	4
SZ15	HFIP-H ₂ O-NaOH	HFIP: 36.2 H ₂ O: 63.7 NaOH: 0.062	$x_{HFIP} = 0.057$ $x_{H_2O} = 0.9422$ $x_{NaOH} = 0.0041$	$c_{HFIP} = 2.49$ $c_{H_2O} = 40.93$ $c_{NaOH} = 0.02$	7
SZ16	HFIP-H ₂ O-NaBPh ₄	HFIP: 43.4 H ₂ O: 55.2 NaBPh ₄ : 1.41	$x_{HFIP} = 0.0776$ $x_{H_2O} = 0.9208$ $x_{NaBPh_4} = 0.0012$	$c_{HFIP} = 3.13$ $c_{H_2O} = 37.2$ $c_{NaBPh_4} = 0.05$	6
SZ17	HFIP-H ₂ O-NaBPh ₄	HFIP: 41.6 H ₂ O: 53 NaBPh ₄ : 5.41	$x_{HFIP} = 0.0773$ $x_{H_2O} = 0.918$ $x_{NaBPh_4} = 0.00494$	$c_{HFIP} = 3.13$ $c_{H_2O} = 37.2$ $c_{NaBPh_4} = 0.199$	7
SZ18	HFIP-H ₂ O-C ₂₄ H ₂₀ PCl	HFIP: 39.6 H ₂ O: 49.8 TPHP+Cl ⁻ : 10.9	$x_{HFIP} = 0.0773$ $x_{H_2O} = 0.913$ $x_{TPHP+Cl^-} = 0.01$	$c_{HFIP} = 3.15$ $c_{H_2O} = 37.17$ $c_{TPHP+Cl^-} = 0.394$	3
SZ19	HFIP-H ₂ O-C ₂₄ H ₂₀ PCl	HFIP: 40.3 H ₂ O: 51.2 TPHP+Cl ⁻ : 8.5	$x_{HFIP} = 0.0772$ $x_{H_2O} = 0.916$ $x_{TPHP+Cl^-} = 0.00722$	$c_{HFIP} = 3.13$ $c_{H_2O} = 37.2$ $c_{TPHP+Cl^-} = 0.29$	3

Sample	Components	Mass %	Molbrüche x	concentration molL ⁻¹	pH
SZ20	H ₂ O-NaOH	H ₂ O:99.94 NaOH:0.06	$x_{\text{H}_2\text{O}} = 0.99973$ $x_{\text{NaOH}} = 0.00027$	$c_{\text{H}_2\text{O}} = 55.59$ $c_{\text{NaOH}} = 0.015$	12

Table 3.1.: Overview of samples including components, weight percentages, mole fractions, concentrations, and measured pH values

4. Results

The following section presents the results of the experimental investigations. For clarity, the sample names used throughout this chapter correspond directly to those listed in the sample overview provided in the Table 3.1. The analysis of the data focuses on their physical interpretation and was carried out using a combination of fitting functions and subsequent evaluation of the obtained parameters. To ensure a systematic presentation, the results are organized according to the specific components of the samples, allowing for a direct comparison of the influence of different constituents on the structural behavior of the investigated systems.

4.1. Overview

The measurements analyzed in this chapter were performed with acquisition times of either 600 s or 1500 s per temperature step, covering a q -range of $0.08\text{--}3\text{ nm}^{-1}$ for SAXS and $0.8\text{--}12\text{ nm}^{-1}$ for WAXS. The measuring times could be reduced owing to the high sensitivity and good statistics of the detector. For all experiments, the temperature was varied from $10\text{ }^{\circ}\text{C}$ to $96\text{ }^{\circ}\text{C}$ in increments of $2\text{ }^{\circ}\text{C}$. The measurements were automated and controlled by the macro described in section A.3, which defined the scan times, temperature sequence, and sample positions.

All samples were sealed and measured in the temperature-controlled holder shown in Figure 3.4, which minimized HFIP evaporation during the experiments. To monitor possible changes in sample stability, selected measurements were repeated after defined time intervals; repeated datasets are indicated by different markers in the following plots. The scattering intensities obtained for HFIP-water mixtures are consistent with the results reported by [47], where the maximum intensity was found at a mole fraction of $x_{\text{HFIP}} = 0.071$ in D_2O . In agreement with these findings, the present data show that between $x_{\text{HFIP}} = 0.071$ and $x_{\text{HFIP}} = 0.089$ the scattering intensity gradually decreases, reflecting the sensitivity of the system to small compositional changes.

The raw data is corrected by three different functions, a solid angle correction, a distance correction and a polarization correction. The detector geometry causes the effective solid angle to vary with the scattering angle 2θ . This can be corrected by applying a factor which normalizes the measured intensity to the angle independent scattering intensity.[43]

$$I_{\text{corr}} = I_{\text{meas}} \cdot \cos^3(2\theta), \quad (4.1)$$

The intensity recorded on the detector decreases with the square of the sample detector distance R . To correct for geometric beam spreading, a factor is applied, ensuring that

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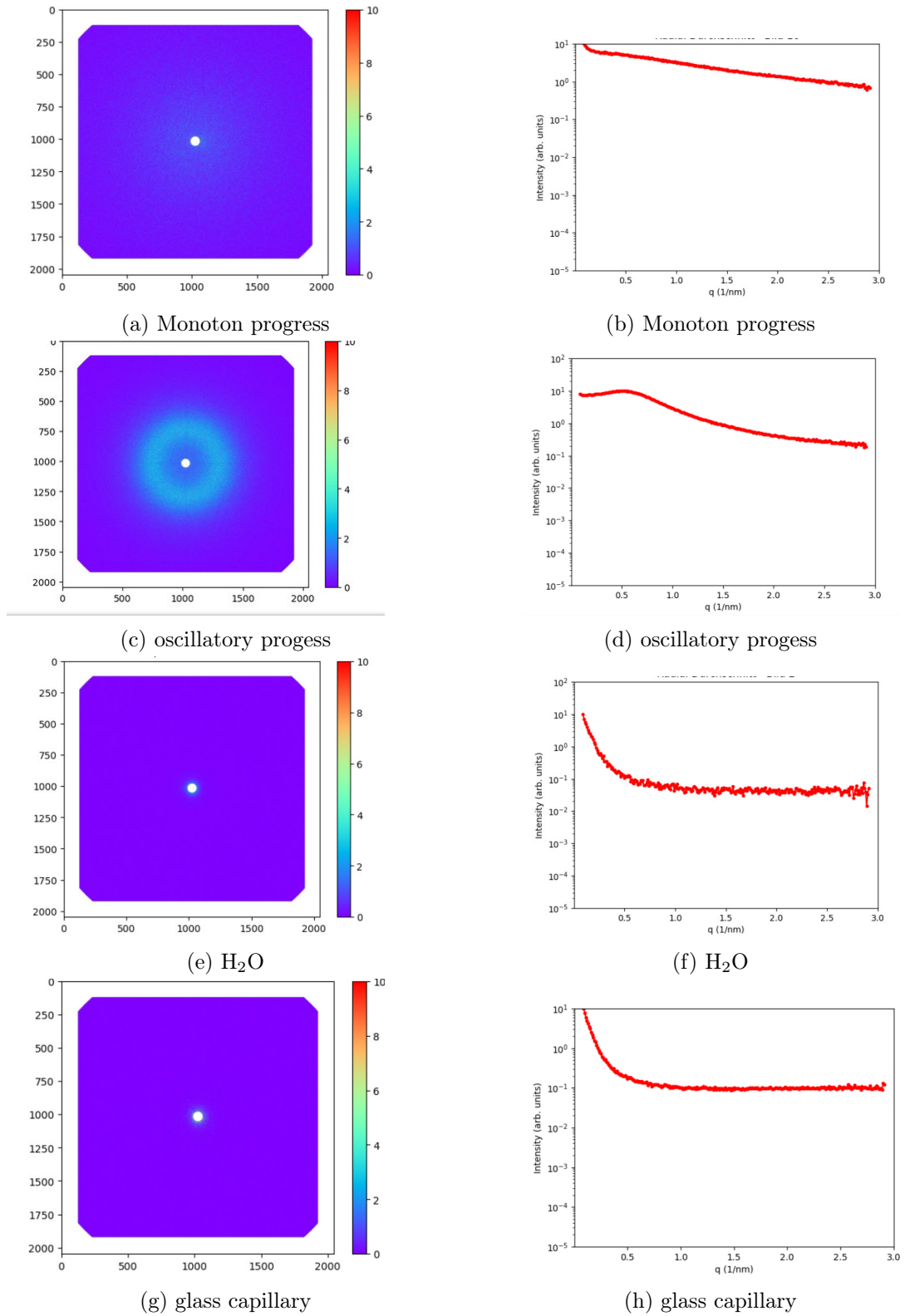


Figure 4.1.: Left: in $68\mu\text{m}$ pixel coordinates.

Right: Normalized Intensity by transmitted intensity, exposure and the corrections from [43] versus q (nm^{-1}).

data taken at different sample-detector distances are directly comparable.[43]

$$I_{\text{corr}} = I_{\text{meas}} \cdot \frac{1}{R^2} \quad (4.2)$$

Due to the partially polarized X-ray beam the angular distribution of the scattered intensity is influenced. This effect is accounted for by a polarization factor where 2θ is the scattering angle, ϕ is the azimuthal angle, and f is the polarization factor (typically $f = 0.9\text{--}0.99$ for synchrotrons and $f = 0$ for conventional X-ray tubes). This correction removes distortions arising from anisotropic polarization.[43]

$$P(2\theta, \phi, f) = \frac{1}{2} [1 + \cos^2(2\theta) - f \cos(\phi) \sin^2(2\theta)] , \quad (4.3)$$

Figure 4.1 shows 2D detector images with their corresponding radial middled Intensity plots. Figure 4.1a and Figure 4.1b show a monoton progress in the set of data. The 2D image schos no sgnificant rings but a kind of diffuse pattern of lighter spots. Also th corresponding corrected and middled intensity plot shows a monoton behavior. An example for a 2D pattern including a sharp ring, can be seen in Figure 4.1c. The radial middled and corrected intensity shows a peak at the position of the ring in the 2D images. The 2D images of water in Figure 4.1e shows in contrast to Figure 4.1a no big diffuse pattern of light spots. The light spots are mor positioned close around the masked beam stop. The rest of the diffuse pattern is very weak in signal. Due to this the radial middles Intensity is also around 1 up to 2 orders of magnitude smaller than in Figure 4.1b and Figure 4.1d. The same hapens for the 2D images and radial middles intensity plot of the empty glass capillary, which can be seen in Figure 4.1g and Figure 4.1h. But the signal from 1.5 mm water is stronger than the signal from $2 \times 10 \mu\text{m}$ empty glass capillary.

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4.2. HFIP-Water

The samples consisting of HFIP and water are labeled SZ7 to SZ10, with their compositions listed in Table 3.1. The following plots present measurements of these samples taken at different time intervals. When comparing the HFIP concentrations, the ascending order is SZ9, SZ8, SZ7, SZ10, and SZ11. Due to discrepancies in the data, sample SZ11 was not evaluated using the Ornstein-Zernike model.

These repeated measurements are indicated by different markers in the plots. Sample SZ7 with $x_{\text{HFIP}} = 0.0778$ exhibits the highest scattering intensity.

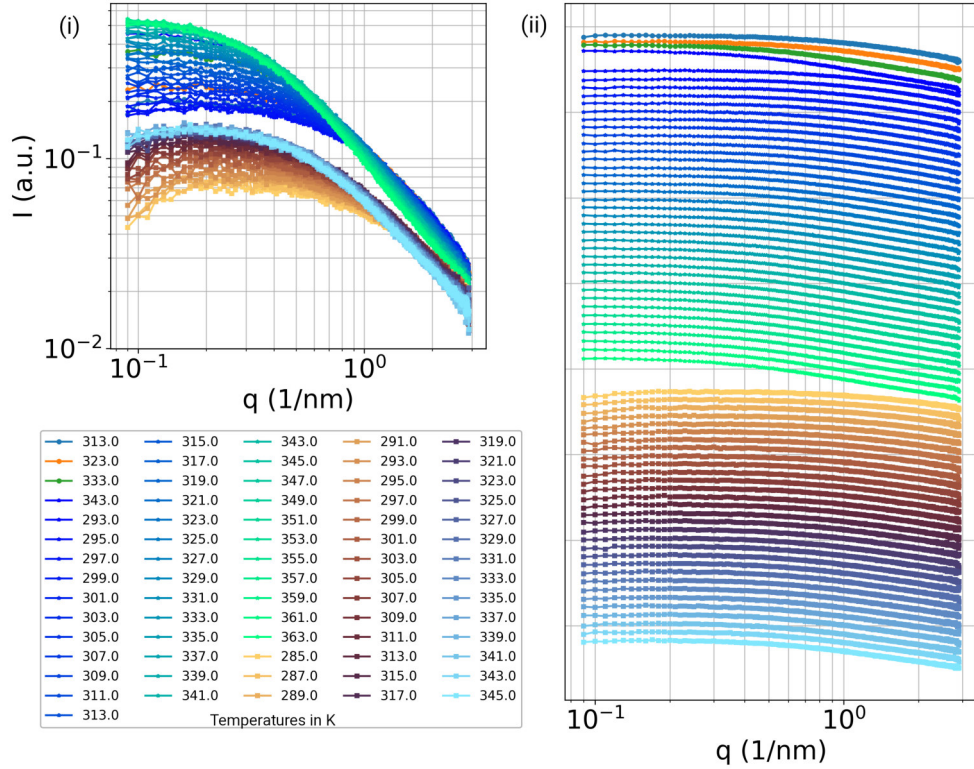


Figure 4.2.: Background-corrected small-angle X-ray scattering (SAXS) intensity $I(q)$ as a function of the scattering vector q for a series of temperatures (in K) for three measurements of sample SZ7, indicated by different markers. SZ7 contains $x_{\text{HFIP}} = 0.0778$ and $x_{\text{H}_2\text{O}} = 0.9222$.

The measurements marked with circles and stars were performed on August 4, while the square markers correspond to measurements carried out 24 days later. (i) Data plotted on a logarithmic scale.

(ii) Waterfall representation of the same background-corrected data.

SZ7 shows two measurements with a distance of 20 days. On the left hand side, one can see that the intensity is changing. The measurement taken 20 days later shows a

decrease in intensity of about 0.5 orders of magnitude. Several factors may account for the observed change in intensity. Since HFIP is highly volatile with a boiling point of only about 58 °C, even minor losses due to evaporation or permeation can shift the HFIP:H₂O ratio, thereby altering the optical properties of the sample. Figure A.1 shows an image of a capillary filled with pure HFIP in which white deposits have formed at the top of the capillary near the closure. In addition, under certain conditions this volatility may even lead to partial distillation, further changing the relative composition of the mixture. Another important factor is the protonation state of the system, HFIP acts as a strong hydrogen-bond donor, and the uptake of atmospheric CO₂ lowers the pH. Changes in protonation and deprotonation equilibria can therefore modify the molar extinction coefficient and quantum yield.[2] Finally, the aggregation state of the analyte may vary over time. HFIP is known to destabilize, denature, or dissolve aggregates. Thus, with ongoing storage or altered mixing ratios, different aggregation or disaggregation behavior may occur, leading to further variations in the measured intensity.

The progression of the scattering curves can be described in detail. Starting from the high- q region, all curves show an almost linear increase, while around 0.5 nm^{-1} a noticeable bending sets in. Towards the low- q end of the measurement $\sim 0.01 \text{ nm}^{-1}$, the older datasets level off linearly, whereas the more recent measurements exhibit a slight curvature. This provides further evidence for evaporation within the sample, as it can lead to density fluctuations that have a pronounced effect particularly in the low- q regime. This nearly linear trend, consistent with Ornstein-Zernike-type correlations and a finite correlation length in the system. The background (capillary scattering normalized by its transmission) was subtracted, and the data were masked around the beamstop to eliminate spurious contributions from parasitic scattering. These corrections strongly support a physical origin of the observed plateau. Nevertheless, instrumental factors such as limited resolution or residual beam divergence may still contribute to a partial flattening, and should therefore be kept in mind when interpreting the small- q regime.

In contrast, SZ8 exhibits a different behavior. The measurements performed 23 days apart show no loss of intensity compared to the earlier dataset. This suggests that the capillary seal was tighter, preventing evaporation. Since the sealing method was changed from heat-shrink tubing to UV adhesive, this difference must be taken into account as a possible explanation. Starting from the high- q region, all curves show an almost linear increase, while around 0.5 nm^{-1} a noticeable bending sets in. Towards the low- q end of the measurement $\sim 0.01 \text{ nm}^{-1}$, the datasets level off linearly.

SZ9 again shows a significant intensity loss for the measurement after 20 days. it is again around 0.5 orders of magnitude. This again shows, that also the new closure method with the glue is possible not completely closing the capillary up. For SZ10 only one measurement was performed. Due to this, there can not be any aussagen about the elding process of the sample. But one can see, that the intensity curves following the Ornstein-Zernike Model which is indicated in Figure 4.7c For the analysis of samples SZ7-SZ10, the Ornstein-Zernike (OZ) model was applied. The theoretical background and derivation are described in detail in section 2.8. Figure 4.7d shows the theoretical Ornstein-Zernike curve (red), which exhibits a slope of $q \sim -2$. The blue curve corresponds exemplarily to

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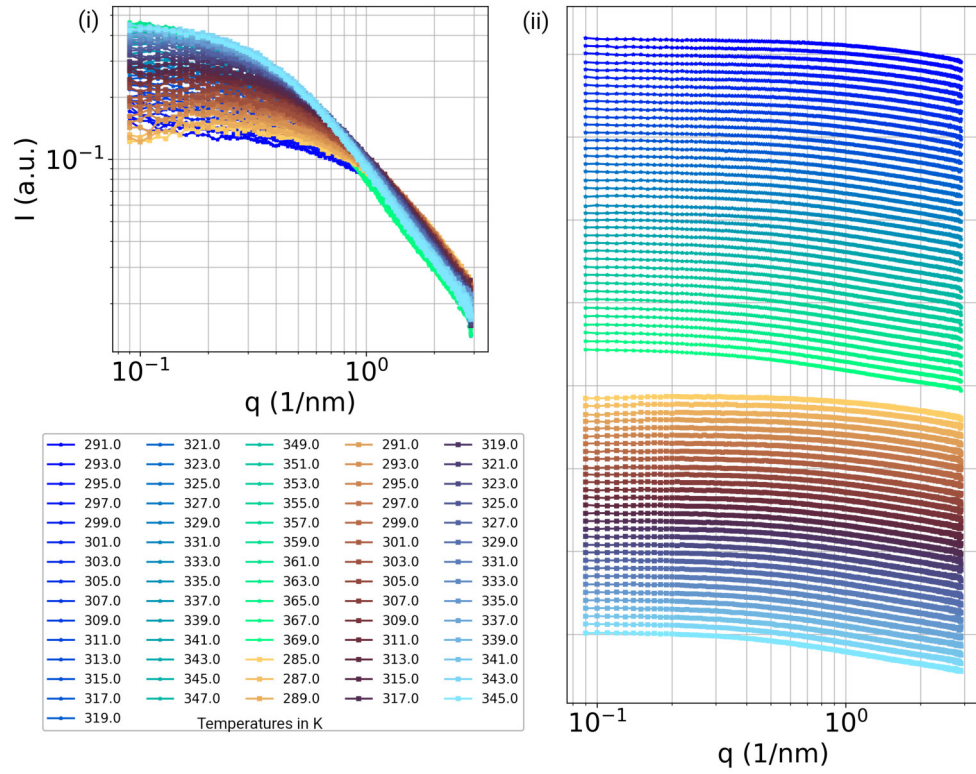


Figure 4.3.: Background corrected small-angle X-ray scattering (SAXS) intensity $I(q)$ as a function of the scattering vector q for a series of temperatures in K for three measurements, indicated by the different markers, of the sample SZ8. SZ8 contains $x_{HFIP} = 0.065$ and $x_{H_2O} = 0.935$. The measurements with star marker was performed on the 5th of august, while the squer marked measurement were 23 days later performed.

(i) Data plotted on a logarithmic scale.

(ii) Waterfall representation of the same background-corrected data.

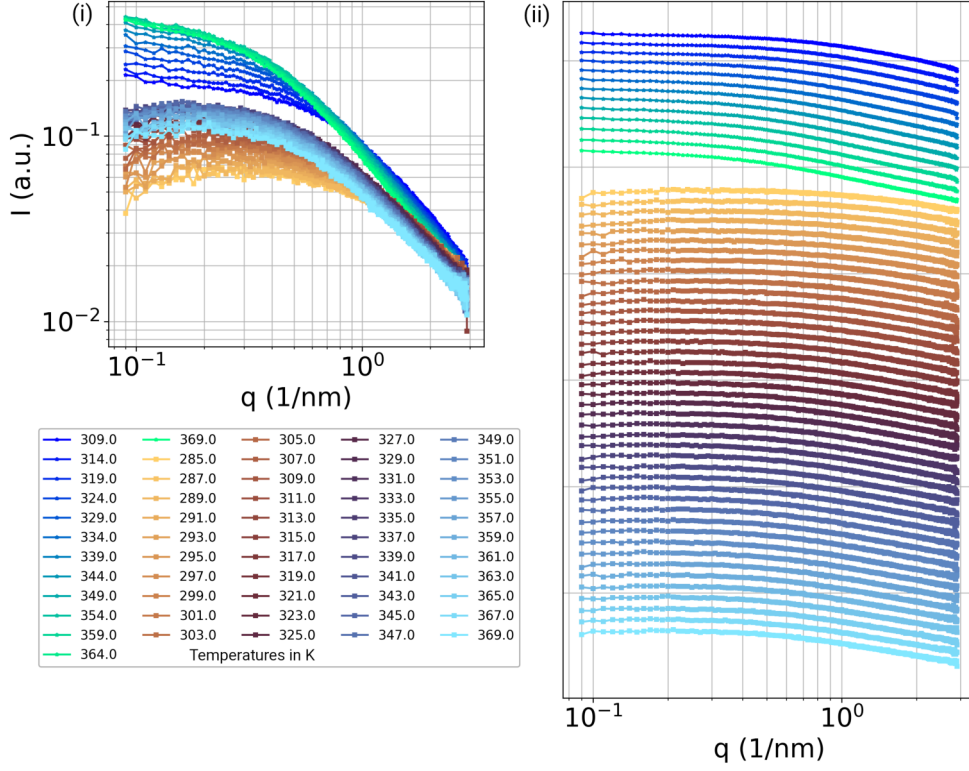


Figure 4.4.: Background corrected small-angle X-ray scattering (SAXS) intensity $I(q)$ as a function of the scattering vector q for a series of temperatures in K for two measurements, indicated by the different markers, of the sample SZ9. SZ9 contains $x_{\text{HFIP}} = 0.055$ and $x_{\text{H}_2\text{O}} = 0.945$. The measurements with star marker were performed on the 5th of August, while the square marked measurements were 20 days later performed.

(i) Data plotted on a logarithmic scale.

(ii) Waterfall representation of the same background-corrected data.

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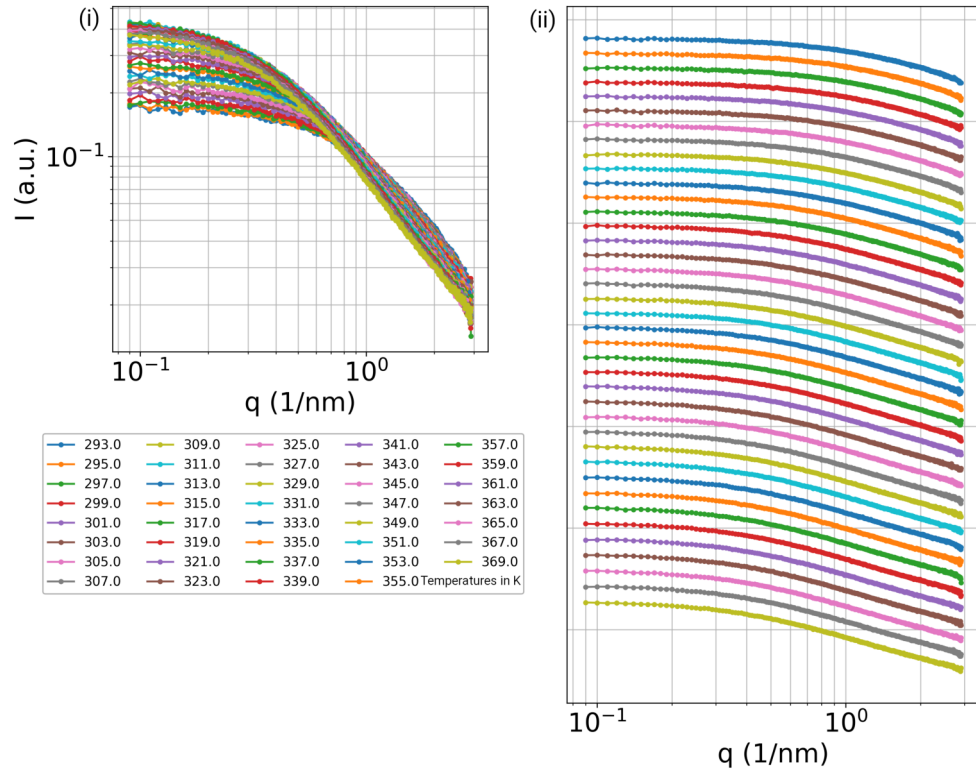


Figure 4.5.: Background corrected small-angle X-ray scattering (SAXS) intensity $I(q)$ as a function of the scattering vector q for a series of temperatures in K for one measurement, of the sample SZ10. SZ10 contains $x_{HFIP} = 0.082$ and $x_{H_2O} = 0.918$. The measurement with circular marker was performed on the 10th of august.

- (i) Data plotted on a logarithmic scale.
- (ii) Waterfall representation of the same background-corrected data.

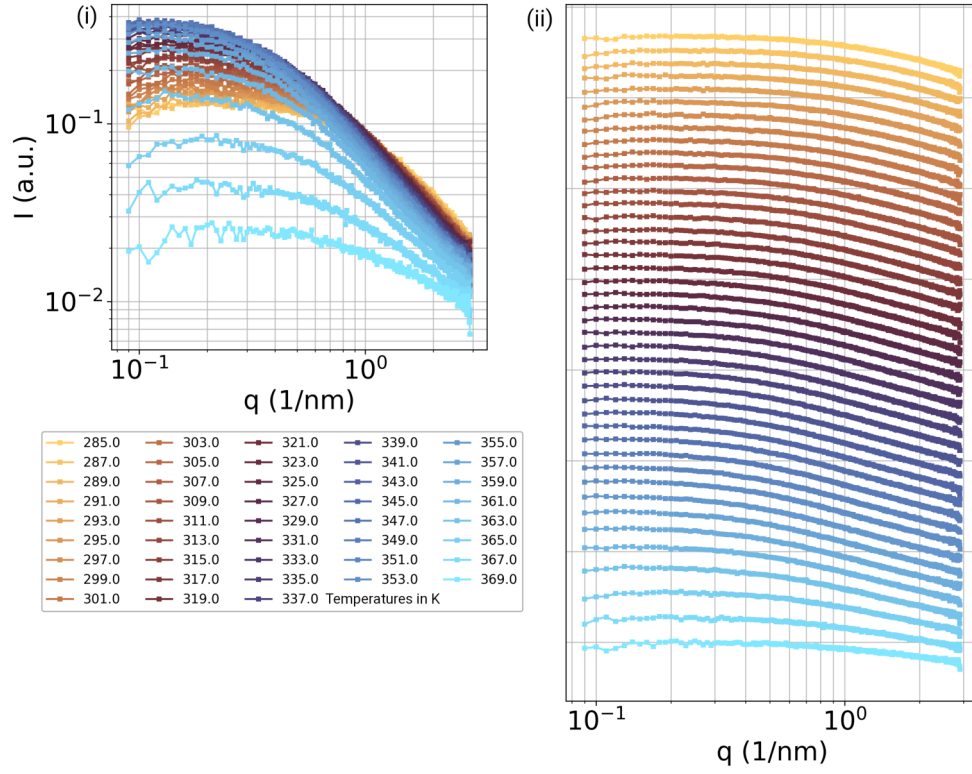


Figure 4.6.: Background corrected small-angle X-ray scattering (SAXS) intensity $I(q)$ as a function of the scattering vector q for a series of temperatures in K for one measurement, of the sample SZ11. SZ11 contains $x_{HFIP} = 0.089$ and $x_{H_2O} = 0.911$. The measurement with circular marker was performed on the 28th of august.

- (i) Data plotted on a logarithmic scale.
- (ii) Waterfall representation of the same background-corrected data.

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the experimental data of sample SZ7.

A comparison with alternative approaches demonstrates that these do not provide an adequate description. A Gaussian model of the form

$$I(q) \propto \exp\left(-\frac{q^2\sigma^2}{2}\right) \quad (4.4)$$

leads to a much steeper decay of the intensity than observed in the measurements due to its exponential dependence. An even stronger decrease is predicted by the Porod law,

$$I(q) \propto q^{-4} \quad (4.5)$$

which describes scattering from sharp interfaces and is therefore not applicable to the present homogeneous liquid phase.[44] A Porod plot, see Figure 4.7b, confirms this, as no plateau is formed in the high- q region.

In contrast, the Ornstein–Zernike model corresponds to a Lorentz function and predicts an intensity decay with q^{-2} . A plot of $I(q)^{-1}$ versus q^2 , see Figure 4.7c, shows a clear linear relationship, confirming the applicability of the OZ formalism. The extracted fit parameters carry direct physical meaning: $I(0)$ represents the amplitude of the density fluctuations, while the correlation length ξ characterizes their spatial extent. Thus, the Ornstein-Zernike model provides the appropriate description of the SAXS data of these HFIP-water mixtures. By using the Ornstein Zernike Model, as mentioned above, the parameters which are given back are the coherence length ξ and the amplitude of the density fluctuations $I(0)$. Analyzing this arameters further one leads to the critical exponents from the 2D/3D Ising model.

Figure 4.8a shows the plots of the coherence length against the temperature for teh samples SZ7-SZ10. the differnt markers in the plot corresponds to measuremnt on doffernt times and the same color corrüonds to the same sample. From Equation 2.22 one gets the critil exponent γ . On the other hand from Equation 2.23 one gets the exponente ν . For the ξ and corresonding χ plot, delta from Equation 2.24, stays the same. The Definition of χ includes $I(q)$ and the temperature T .

$$\chi = \frac{I(q \rightarrow 0)}{T} \quad (4.6)$$

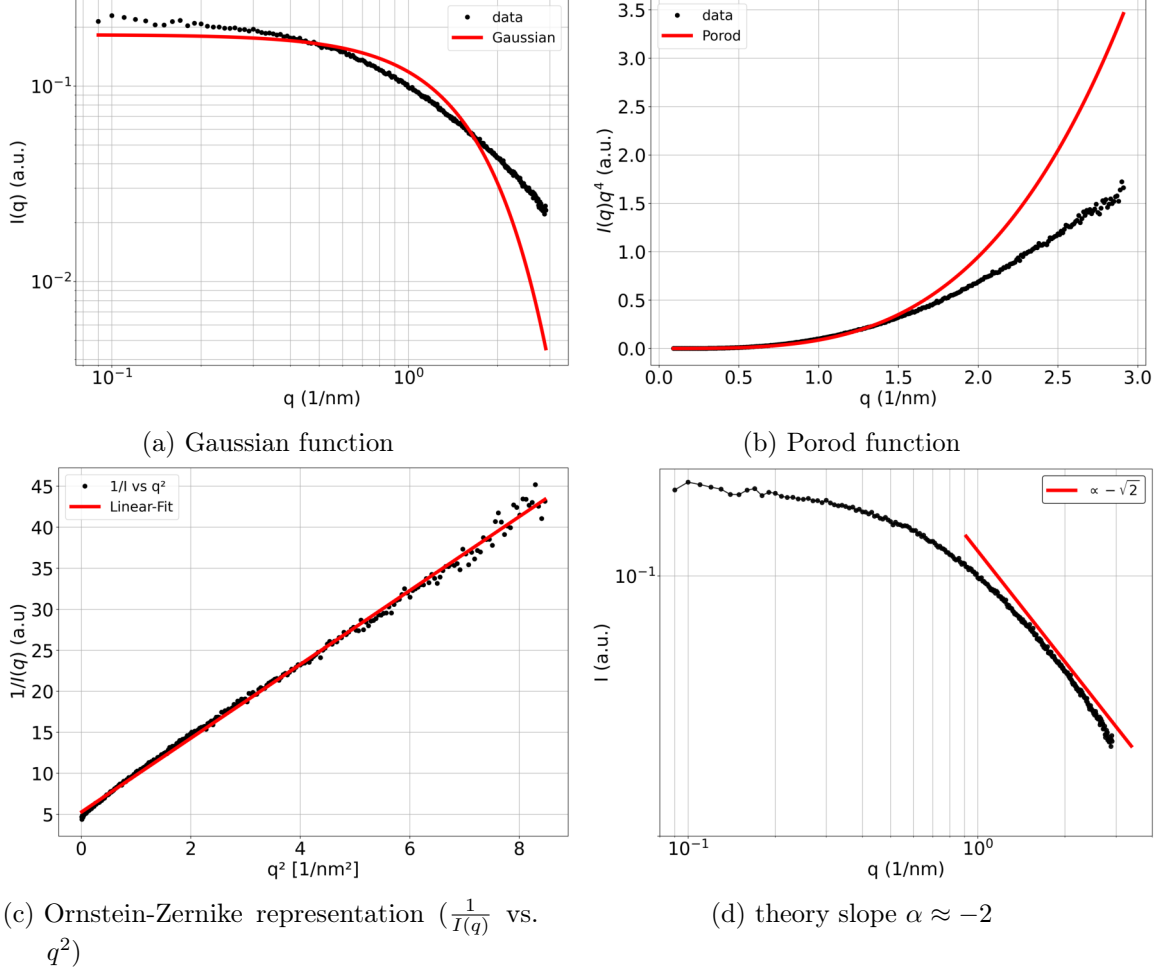


Figure 4.7.: Comparison of different fitting approaches for the analysis of the samples SZ7-SZ10. (a) Fit with a Gaussian function, which decays too steeply compared to the measured data. (b) Fit with a Porod function, which does not capture the experimental trend at higher q -values. (c) Ornstein-Zernike representation ($\frac{1}{I(q)}$ vs. q^2) showing a clear linear relation, consistent with the theoretical prediction. (d) Log-log representation of the data with slope $\alpha \approx -2$, in agreement with the Ornstein-Zernike model.

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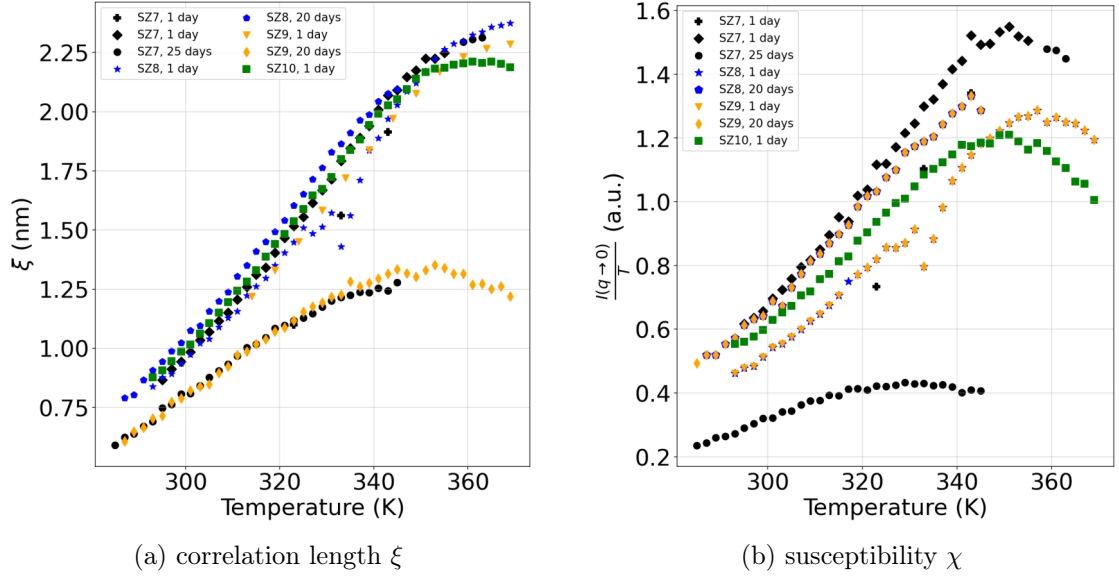


Figure 4.8.: Temperature-dependent analysis of samples SZ7-SZ10 based on Ornstein-Zernike fits. (a) Correlation length ξ as a function of temperature. (b) Susceptibility $\chi = \frac{I(q \rightarrow 0)}{T}$ as a function of temperature. Different symbols correspond to different sample ages and different colors for different HFIP/H₂O concentrations, as indicated in Table 3.1.

The following Table 4.1 includes the critical exponents γ and ν as well as the parameter δ . All of these 3 parameters resulting from the Equation 2.23, Equation 2.24 and Equation 2.22.

Sample	SZ7, 1 day	SZ7, 25 days	SZ8, 1 day	SZ8, 20 days	SZ9, 1 day
γ	2.23	3.61	1.25	2.76	2.46
ν	1.98	3.00	1.16	2.63	1.92
δ	0.144	0.217	0.094	0.180	0.150

Sample	SZ9, 25 days	SZ10, 1 day
γ	3.93	2.43
ν	3.00	2.18
δ	0.224	0.163

Table 4.1.: critical exponents resulting from the fitting process with Equation 2.23, Equation 2.24 and Equation 2.22.

Based on these values, sample SZ8 is the closest to the critical point. It exhibits the smallest δ , which is proportional to the difference between the actual concentration and the critical concentration. Furthermore, the corresponding γ and ν values are in good

agreement with the literature values of the Ising model.

When comparing the progression of the ξ and χ functions for different samples and measurement days, certain trends emerge: older measurements yield larger values of both functions, while repeated measurements after a certain period of time result in smaller values of ξ and χ . Additionally, the critical temperature decreases in the more recent measurements. Notably, only sample SZ8 shows no change in either of these functions. A possible explanation could be the new method of sealing the capillary with UV glue. However, all other samples prepared after SZ8 were also sealed in this way and still exhibit the aging effect. The reasons for this aging process are therefore likely related to the same factors discussed earlier in this section.

Figure 4.9 Shows the scattered und transmitted intensities normalized by the exposure time and I0

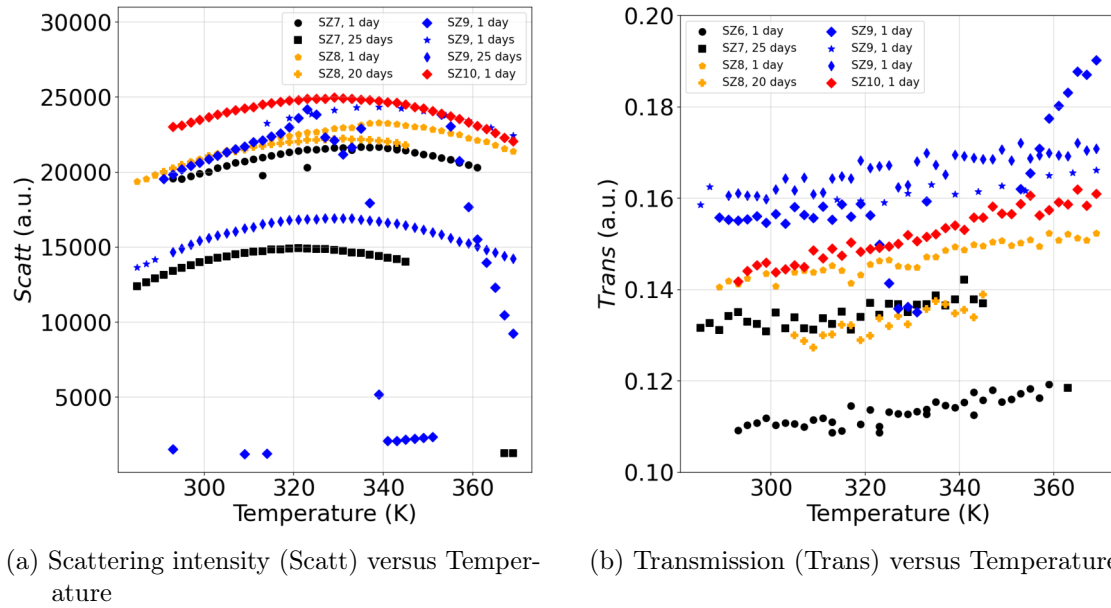


Figure 4.9.: (a) Scattering intensity (Scatt) and (b) Transmission (Trans) as a function of temperature for different samples and sample ages. The Transmission varies between 10 % and 20 %. All samples exhibit an increase in scattering with temperature up to a maximum, followed by a decrease at higher T , consistent with critical-like fluctuations.

Aging effects are clearly visible in the scattering data, particularly for SZ7 and SZ8, where the intensity decreases and the curves flatten after several days. This indicates that the structural correlations within the samples weaken over time. The transmission data shown in Figure 4.9(b) exhibit complementary behavior. transmission generally increases with temperature and reveals systematic differences between the samples, which can be attributed to both composition and aging processes.

The scattering data in Figure 4.9a reveal clear differences in intensity levels. SZ10 exhibits

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the highest absolute scattering, followed by SZ8 and SZ7, while SZ9 shows the lowest intensities. All samples display a similar qualitative trend: scattering increases with temperature, reaches a broad maximum around 320-330 K, and then decreases at higher T , consistent with critical-like fluctuations near an LCST. Aging effects are particularly visible in SZ7 and SZ9: repeated measurements after ~ 20 -25 days yield significantly lower scattering intensities, indicating a loss of HFIP through evaporation or changes in the aggregation state. The transmission data in Figure 4.9b exhibit complementary behavior. In all samples, transmission increases steadily with temperature, reflecting a reduction in turbidity and enhanced homogeneity. SZ9 and SZ10 reach the highest transmission values, whereas SZ7 remains lowest. The aging effect is also evident here, older samples show systematically higher transmission, consistent with the observed reduction in scattering intensity.

Overall one can see, that the SZ7 sample with the optimal HFIP mole fraction, as mentioned earlier, has the smallest Scatt and Trans values for the first measurements. Followed by SZ8 and SZ9 containing lower components of HFIP, the Scatt values are above them of SZ7. The highest Scatt values has SZ10 which contains the highest amount of HFIP. By analyzing the Trans data, SZ9 has the highest values and SZ7 the lowest. So for the Trans data, there is no order for the HFIP mole fraction.

For sample SZ11, the Ornstein-Zernike model fails, as shown in Figure 4.10a. Similarly, the Porod model is not adequate for this dataset. By contrast, the double Lorentz fit shown in Figure 4.10b describes the data very well.

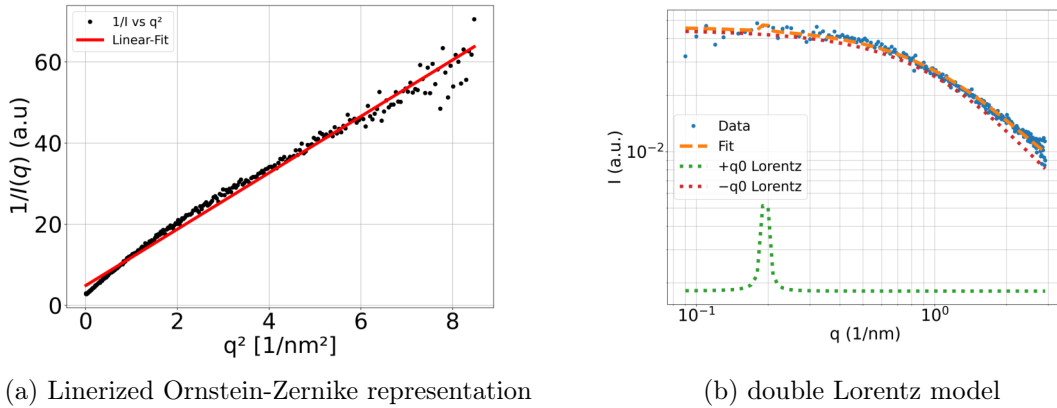


Figure 4.10.: Comparison of different fitting approaches for the analysis of the sample SZ11. (a) Ornstein-Zernike representation ($\frac{1}{I(q)}$ vs. q^2) showing a non clear linear relation. (b) double Lorentz model, consistent with the theoretical prediction.

The use of the double Lorentz model as the fitting function is motivated by the fact that the dataset shows a pronounced intensity loss around 345 K. Moreover, the shape of the intensity curves suggests a peak shift to lower values with increasing temperature. The Ornstein-Zernike model cannot account for this peak shift, which in turn points to a

change in the phase behavior.

An inspection of the 2D scattered image reveals no measurement artifacts, such as bright spots near the beam stop. This confirms that the beam fully illuminates the capillary rather than hitting only part of it. Potential issues such as bubbles within the sample can also be ruled out. Given the reproducibility of the dataset, the occurrence of bubbles is highly unlikely. Figure 4.6 shows just one dataset, but there exists other data from SZ11 that show qualitatively comparable results.

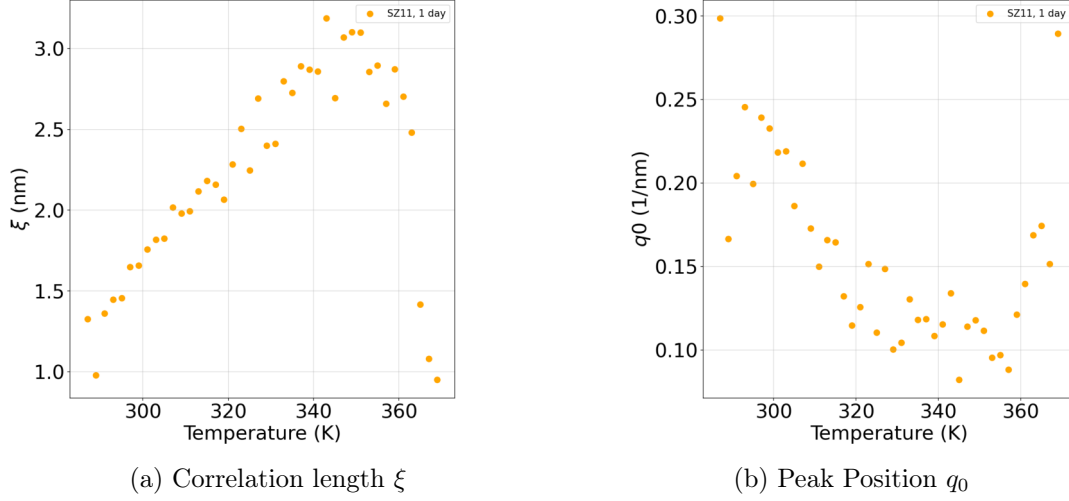


Figure 4.11.: Temperature-dependent analysis of sample SZ11 based on Double Lorentzian fits.

- (a) Correlation length ξ as a function of temperature.
- (b) Peak Position q_0 as a function of temperature.

The temperature dependent analysis reveals two complementary trends. The correlation length ξ Figure 4.11a increases steadily, before slightly leveling off at higher temperatures. This indicates enhanced structural correlations and the formation of larger fluctuation domains upon heating. In contrast, the peak position q_0 Figure 4.11b shifts to lower values with increasing temperature. Such a shift is consistent with the growth of characteristic length scales in the system, in agreement with the observed increase of ξ .

Sample	SZ11
γ	-
ν	0.66
δ	0.053

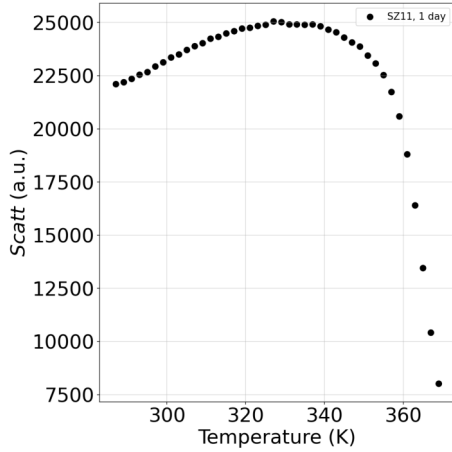
Table 4.2.: critical exponents resulting from the fitting process with Equation 2.23, Equation 2.24 and Equation 2.22.

Table 4.2 includes ν and δ for the sample SZ11. γ could not be estimated for this

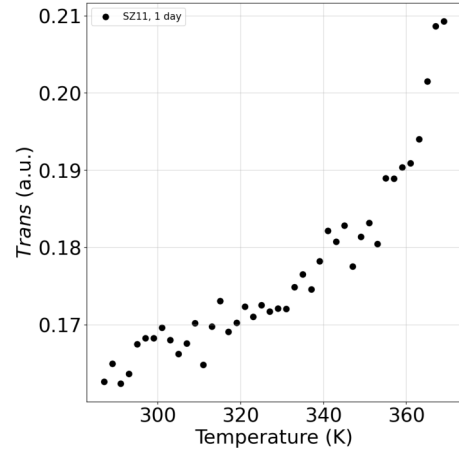
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dataset. Eventhough the estimated values are close to the theoretical values from the Ising model in Equation 2.7. δ is near 0 which means, that the actual concentrations are quite close to the critical concentrations x_c . This is also in good agreement with the data which are shown a atypical phase behavior.

The transmission increases continuously with temperature Figure 4.12a, indicating a gradual reduction of turbidity in the sample. In contrast, the scattering intensity Figure 4.12b exhibits a pronounced maximum around 330 K, followed by a steep decrease at higher temperatures. This behavior is consistent with the presence of critical fluctuations near the LCST, the intensity first rises due to enhanced structural correlations and then drops as the system becomes increasingly transparent.



(a) Scattering intensity (Scatt) versus Temperature



(b) Transmission (Trans) versus Temperature

Figure 4.12.: Temperature dependence of (a) transmission and (b) scattering intensity for the sample SZ11. The transmission increases steadily with temperature, while the scattering shows a clear maximum around 330 K, followed by a sharp decrease. This behavior is characteristic of critical fluctuations near the LCST.

4.3. HFIP-Water-Acid

This section presents the analysis of the samples consisting of HFIP, water, and pentafluoropropionic acid. Sample SZ2 contains a mole fraction of $x_{\text{HFIP}} = 0.039$ and $x_{\text{Acid}} = 0.021$. In comparison to the samples prepared with only HFIP–water mixtures at different concentrations, the HFIP fraction in SZ2 is relatively small. The design of this sample was motivated by SZ1, which contained $x_{\text{HFIP}} = 0.077$ and $x_{\text{Acid}} = 0.001$. That dataset showed no significant effects and exhibited an intensity profile very similar to SZ7. Therefore, the idea was to reduce the HFIP concentration further. Considering the charged components and the donor–acceptor interactions, the HFIP fraction was decreased to $x_{\text{HFIP}} = 0.039$.

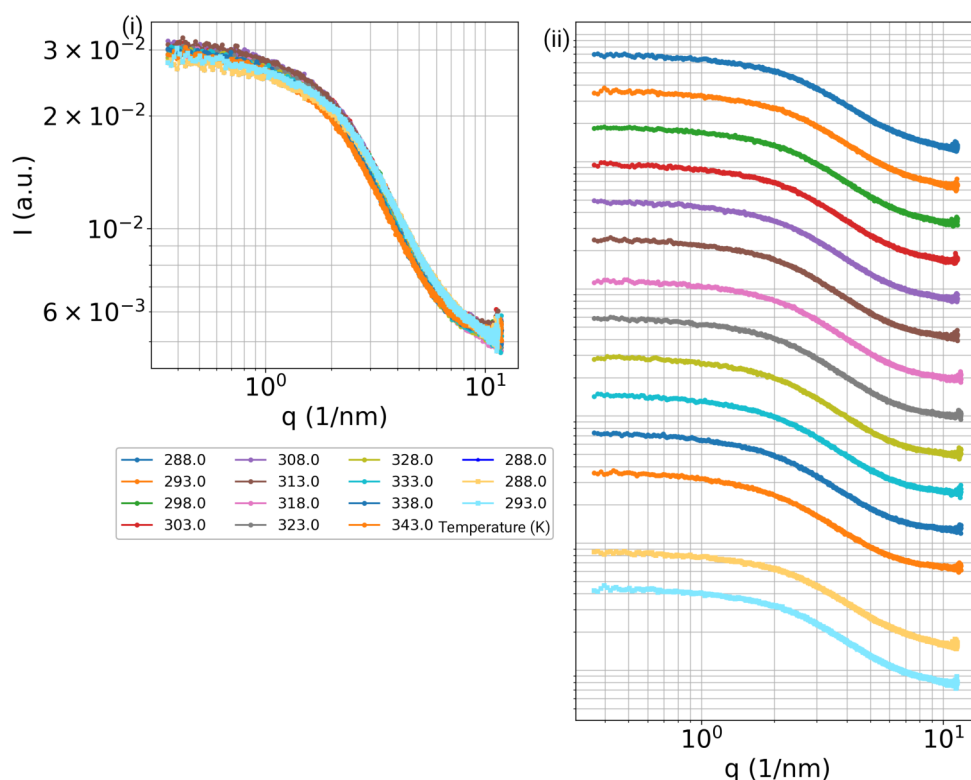


Figure 4.13.: Background corrected small-angle X-ray scattering (SAXS) intensity $I(q)$ as a function of the scattering vector q for a series of temperatures (in K) of the sample SZ2.

- (i) Data plotted on a logarithmic scale
- (ii) Waterfall representation of the same background-corrected data.

Figure 4.13 displays the intensity profile of SZ2, which is about one order of magnitude weaker than that of SZ7. For small q , the intensity is nearly flat, while it starts to decrease slowly around 1 nm^{-1} . Around 2 nm^{-1} the intensity is decreasing faster around a factor of 2. For high q values the intensity is again near a linear behavior.

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To determine the critical exponents, the Ornstein–Zernike (OZ) model was initially applied to the dataset. However, as shown in Figure 4.14a, the plot of $\frac{1}{I(q)}$ versus q^2 does not reveal a linear trend. Therefore, the OZ model cannot be used to describe this dataset. This indicates that the addition of acid influences the system, but its effect is mainly reflected in a general reduction of the scattering intensity and a change in the slope at high q values. The peak position at approximately 1.1 nm^{-1} remains unchanged upon heating or cooling the sample. Alternative fitting models, such as the double Lorentzian or the Voigt profile, are also unsuitable since they fail to capture the steep decay at high q .

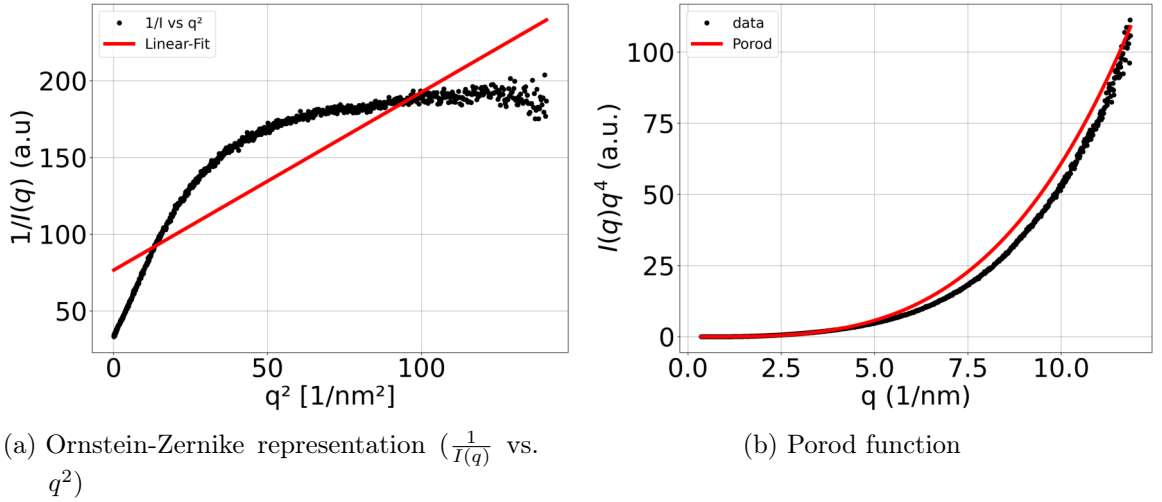


Figure 4.14.: Comparison of different fitting approaches for the analysis of the samples SZ2. (a) Ornstein-Zernike representation ($\frac{1}{I(q)}$ vs. q^2). (b) Fit with a Porod function, which does capture the experimental trend at higher q -values.

Due to some problems with the sample SZ1, the idea was to rising the HFIP mole fraction again and lowering the acid again to $x_{\text{HFIP}} = 0.077$ and $x_{\text{Acid}} = 0.001$. So this is a reproduced SZ1 sample, called SZ5.

Observing the data of SZ5 one can see, that the intensity is now less than for SZ2. So the lowering of the intensity must come from a relationship between the acid and HFIP and can not just be determined by rising the one or the other component within the mixtures. By comparing the intensity process of SZ5 with the one of SZ2 one can see, that the intensity of SZ2 is falling faster for high q . While for SZ5 the intensity is fallen more linearly for high q . The Peak is again around 1.1 nm^{-1} and is stayin for heating or cooling the sample with in the tempreature range of $288 \text{ K} - 324 \text{ K}$. At first the dataset was again fitted with the Ornstein Zernike model, but as expected the model does not fit these type of data. Therefor A double Lorentzian Model was applied which fits the data set quite well. Both SZ5 and SZ2 exhibit an oscillatory trend in their data, suggesting that the corresponding concentrations are not far from a critical point. However, since the peak position remains fixed, no change in the phase behavior of either mixture can

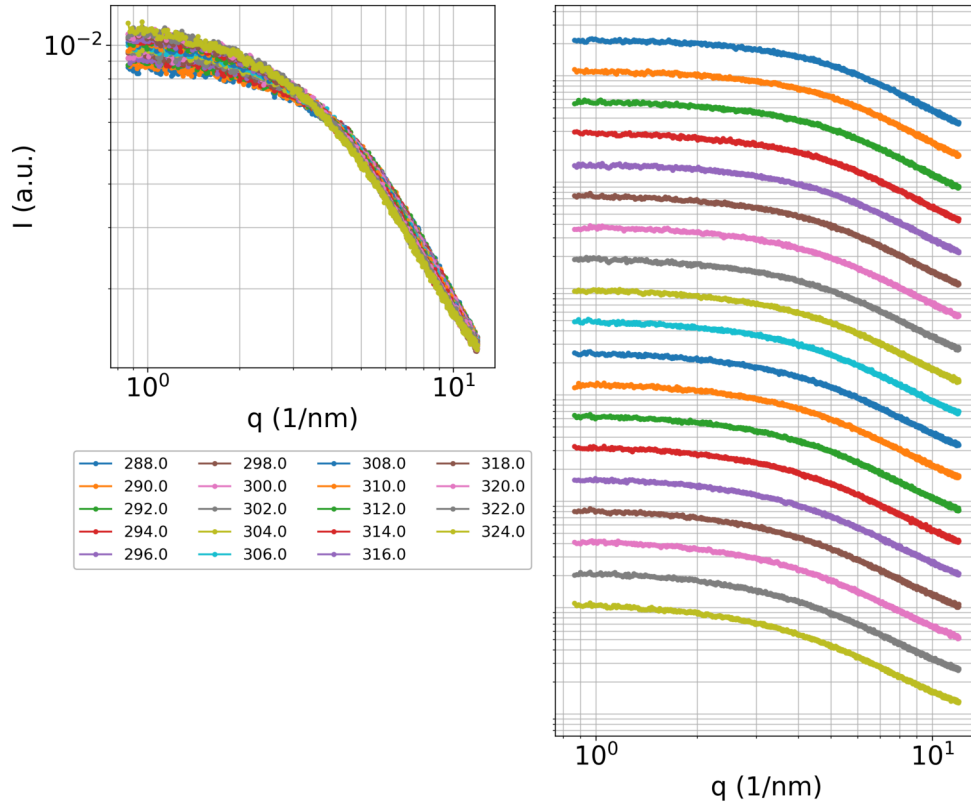


Figure 4.15.: Background corrected small-angle X-ray scattering (SAXS) intensity $I(q)$ as a function of the scattering vector q for a series of temperatures (in K) of the sample SZ5.

- (i) Data plotted on a logarithmic scale
- (ii) Waterfall representation of the same background-corrected data.

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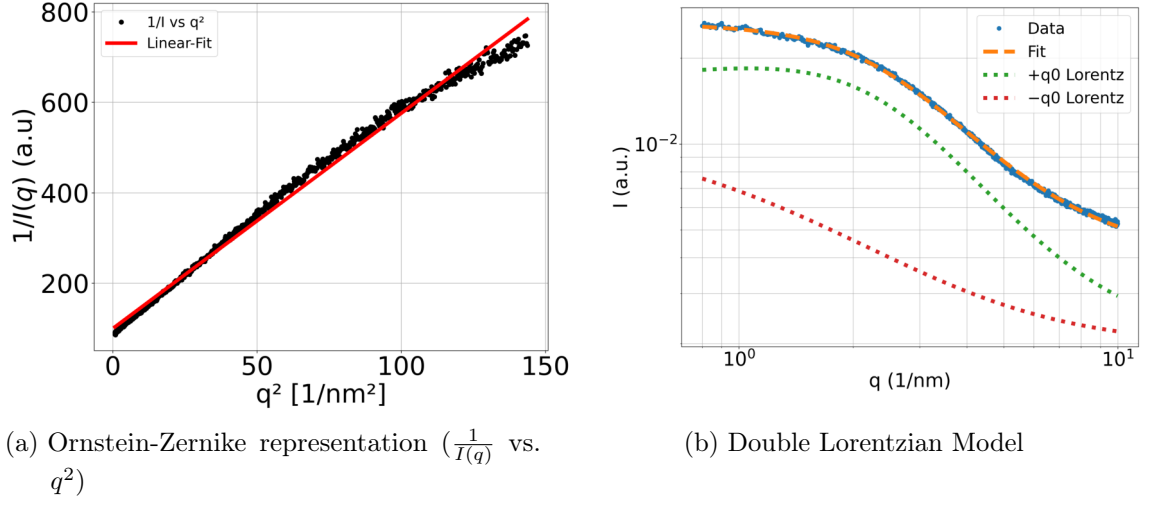


Figure 4.16.: Comparison of different fitting approaches for the analysis of the samples SZ2. (a) Ornstein-Zernike representation ($\frac{1}{I(q)}$ vs. q^2). (b) Double Lorentzian Model with peaks at $\pm q_0$.

be observed. The inability to apply the Ornstein–Zernike model indicates that more than one characteristic process is present within these mixtures, which complicates their description by a single correlation length.

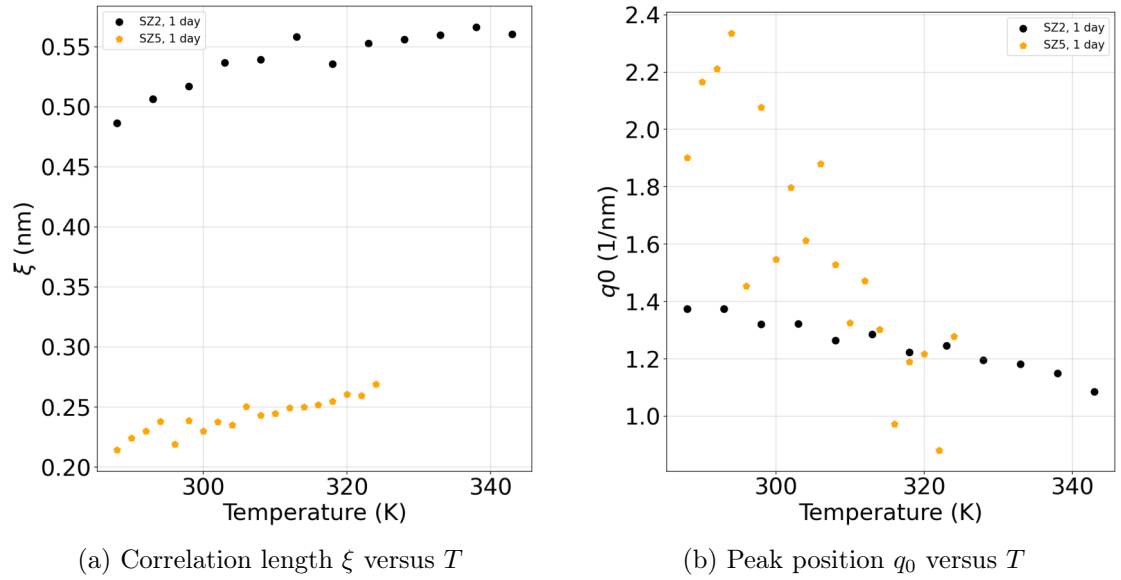


Figure 4.17.: (a) Correlation length ξ as a function of temperature for samples SZ2 and SZ5. (b) Peak position q_0 as a function of temperature for SZ5.

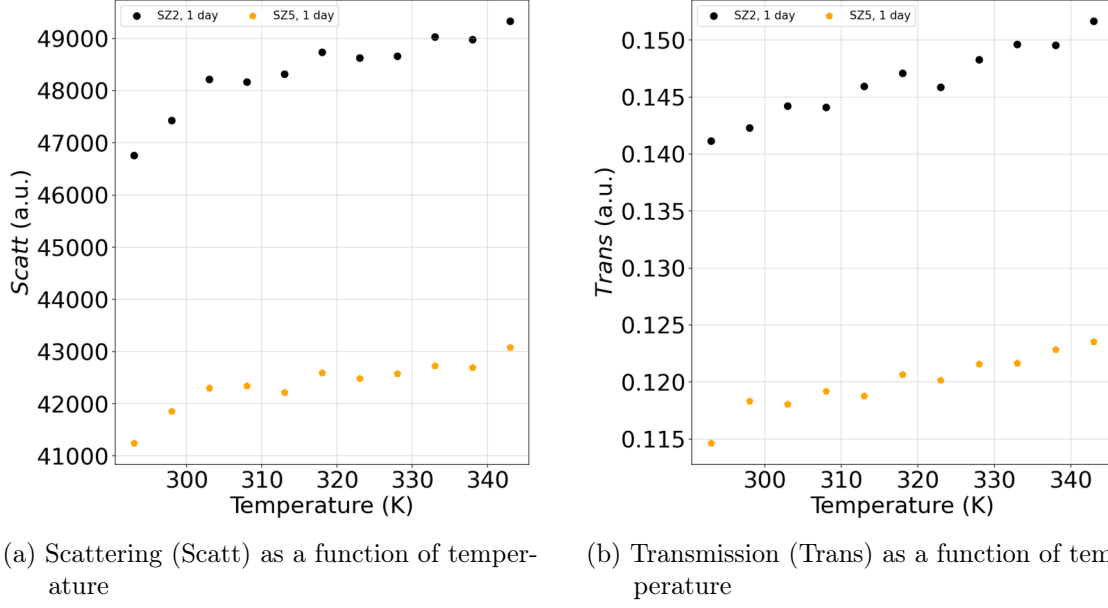


Figure 4.18.: (a) Scattering intensity (Scatt) and (b) Transmission (Trans) as a function of temperature for samples SZ2 and SZ5.

Sample	SZ2, 1 day	SZ5, 1 day
ν	2.9	3.0
δ	0.867	0.99

Table 4.3.: critical exponents resulting from the fitting process with Equation 2.23, Equation 2.24 and Equation 2.22 for SZ2 and SZ5.

The scattering intensity of SZ2 is consistently higher. With increasing temperature, the intensity rises slightly in both cases, with SZ2 showing a more pronounced increase. This suggests stronger structural correlations and denser fluctuations in SZ2 compared to SZ5. The transmission also shows a continuous increase with temperature. SZ2 starts at a higher level ~ 0.141 and reaches about 0.151 at 343 K, while SZ5 increases from ~ 0.115 to about 0.124. The parallel trends indicate a gradual homogenization of both samples with temperature, while the absolute differences can be attributed to differences in composition.

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4.4. HFIP-Water-Acid-Sodium Hydroxide

In the search for a system that exhibits both an LCST and a UCST, the approach was to neutralize the mixtures with NaOH. The pH values of the pure HFIP-water samples were around 5-6, while SZ2 and SZ5 showed strongly acidic conditions with $\text{pH} \approx 1$. SZ3, in contrast, contained an excess of NaOH, resulting in an alkaline pH of about 10. SZ4, on the other hand, was insufficiently neutralized and remained highly acidic with $\text{pH} \approx 0$.

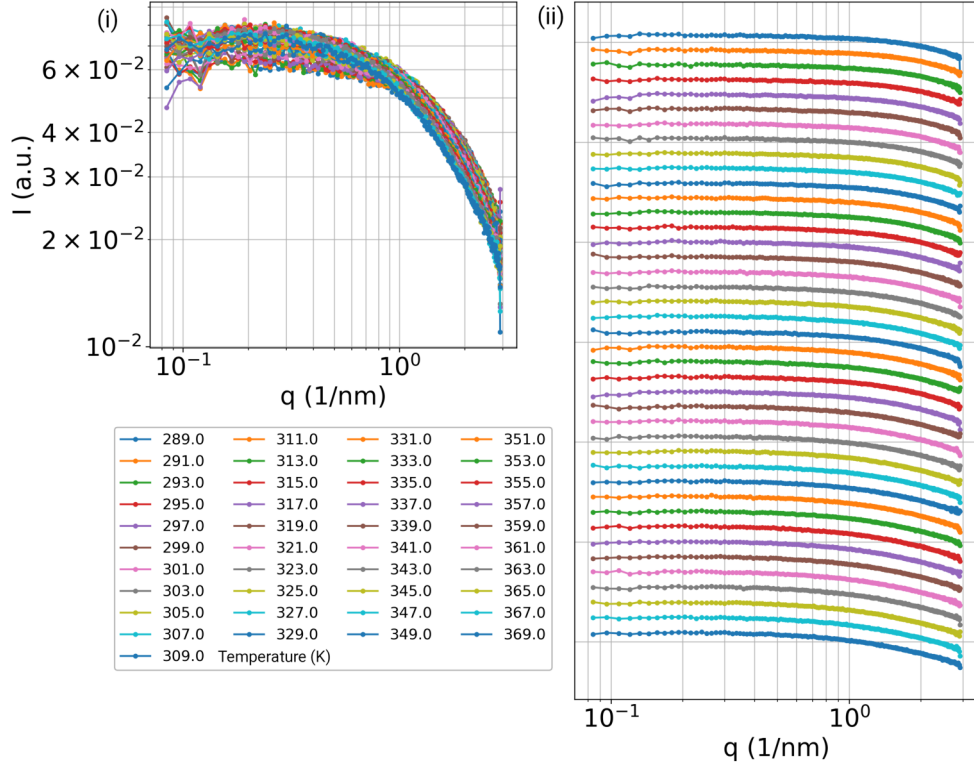


Figure 4.19.: Background corrected small-angle X-ray scattering (SAXS) intensity $I(q)$ as a function of the scattering vector q for a series of temperatures (in K) of the sample SZ6.

- (i) Data plotted on a logarithmic scale with corresponding fits
- (ii) Waterfall representation of the same background-corrected data.

The sample SZ6 was prepared and analyzed at a neutral pH of 7. Its composition was $x_{\text{HFIP}} = 0.0772$, $x_{\text{Acid}} = 0.0096$, and $x_{\text{NaOH}} = 0.01$, such that the acid was fully neutralized by NaOH. The NaOH solution used for sample preparation had a concentration of 1 mol L^{-1} . The scattering intensity profile of SZ6 shows a very flat course, even at higher q -values, with only a weak peak around 1 nm^{-1} . As a result of neutralization, the overall intensity rises again, but remains about half an order of magnitude lower compared to the HFIP-water mixtures. Interestingly, the addition of acid appears to have

induced structural changes in the system: after neutralization, the intensity would be expected to return to the same level as SZ7, since SZ7 corresponds to the original mixture from which SZ6 was prepared.

Due to the flat porgeess of the intensity pattern, the Ornstein Zernike Model was applied. Figure 4.20a shows the Ornstein-Zernike representation ($\frac{1}{I(q)}$ vs. q^2) which shwoing a clear linear relation for SZ6.

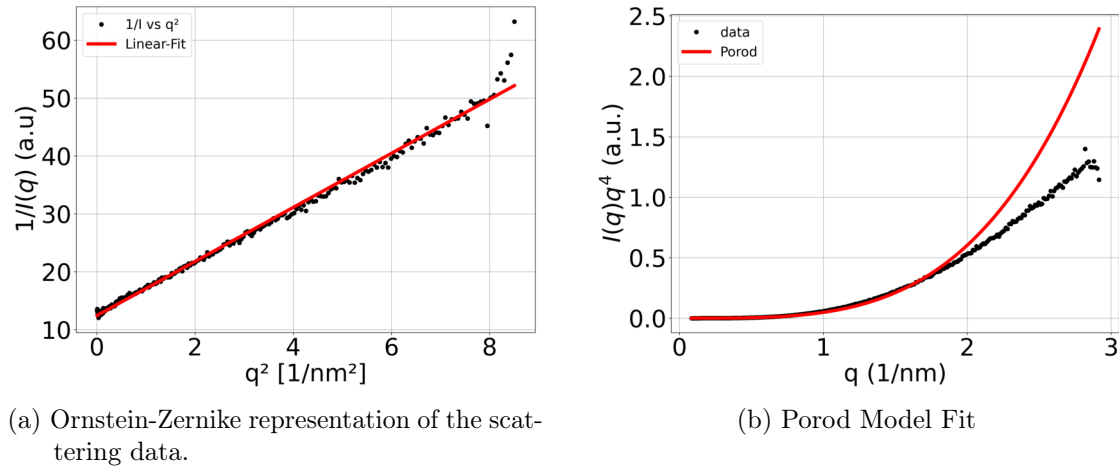


Figure 4.20.: Comparison of different fitting approaches for the analysis of the samples SZ6. (a) Ornstein-Zernike plot of $1/I(q)$ versus q^2 with clear linear relation. (b) Porod Model .

In Addition the Porod Model is used for analyzation of the data. For small q , the Model predicts the data quite well, but for high q the data is derverging from the Porod plot. The somparsion with the Porod plot is included, due to the second dataset of SZ4. This samples follows the Porod theory.

SZ4 contains $x_{\text{HFIP}} = 0.03$, $x_{\text{Acid}} = 0.0017$ and $x_{\text{NaOH}} = 0.013$. Eventhoug the sample is not neutralizes, the data is analyzed. By mixing the HFIP-water-acid mixture with NaOH, it is unforunatley get to much NaOH within the mixture due to the very small amount of NaOH. And a very small amount of NaOH leads to a shift in the pH value. Figure 4.21 shows the WAXS data of the sample SZ4. In comparsion to SZ6 the intensity is shrinking by the factor of 0.5. The reason for this is on one hand the action of the Acid and of NaOH, on the other hand the shrinked amount of HFIP within the sample.

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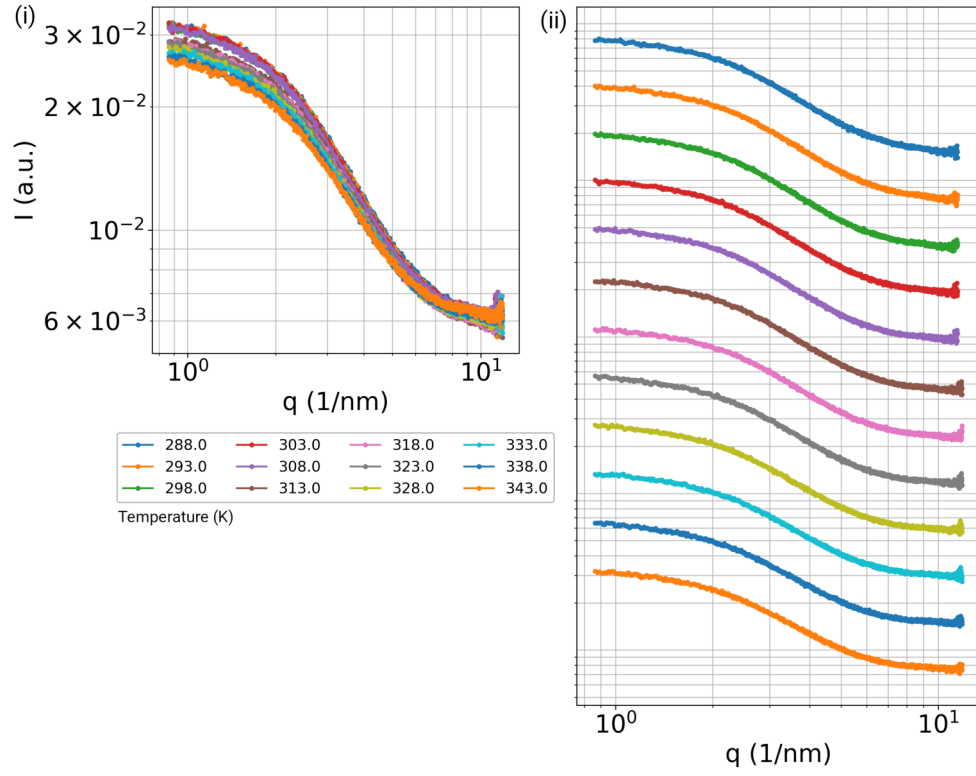


Figure 4.21.: Background corrected wide-angle X-ray scattering (WAXS) intensity $I(q)$ as a function of the scattering vector q for a series of temperatures (in K) of the sample SZ4.

- (i) Data plotted on a logarithmic scale with corresponding fits
- (ii) Waterfall representation of the same background-corrected data.

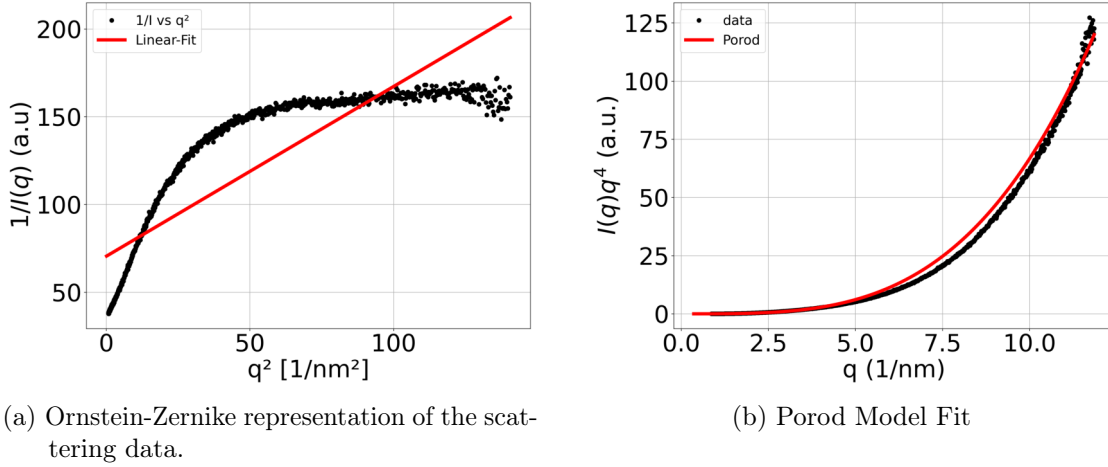


Figure 4.22.: Comparison of different fitting approaches for the analysis of the samples SZ4. a) Ornstein-Zernike plot of $1/I(q)$ versus q^2 with no clear linear relation. (b) Porod Model with clear agreement with the data.

The correlation length ξ increases steadily with temperature from about 0.3 nm to nearly 0.7 nm, indicating a continuous growth of structural correlations in the system. The susceptibility $I(q \rightarrow 0)/T$ decreases monotonically with rising temperature, showing that the scattering strength at small q is gradually reduced. Taken together, the opposing trends of ξ and susceptibility suggest that although correlation lengths become larger with heating, the overall intensity of fluctuations diminishes, pointing to a gradual homogenization of the sample.

Sample	SZ6	SZ4
γ	0.50	-
ν	2.70	0.55
δ	0.296	0.090

Table 4.4.: critical exponents resulting from the fitting process with Equation 2.23, Equation 2.24 and Equation 2.22 for SZ6.

The γ of SZ4 could not be estimated for this structure of dataset.

The scattering intensity increases steadily with temperature up to about 330 K, where a broad maximum is observed. Beyond this point the intensity decreases again, suggesting the onset of structural changes and reduced density fluctuations at higher temperatures. The transmission shows a gradual increase with temperature across the entire range, indicating a progressive reduction of turbidity. Together, these trends are consistent with critical-like fluctuations near an LCST, where scattering is enhanced up to a transition region and then suppressed as the system becomes more homogeneous. The Scatt values in Figure 4.24a of SZ4 and SZ6 differ by a factor of 2.6. This effect arises due to the differences

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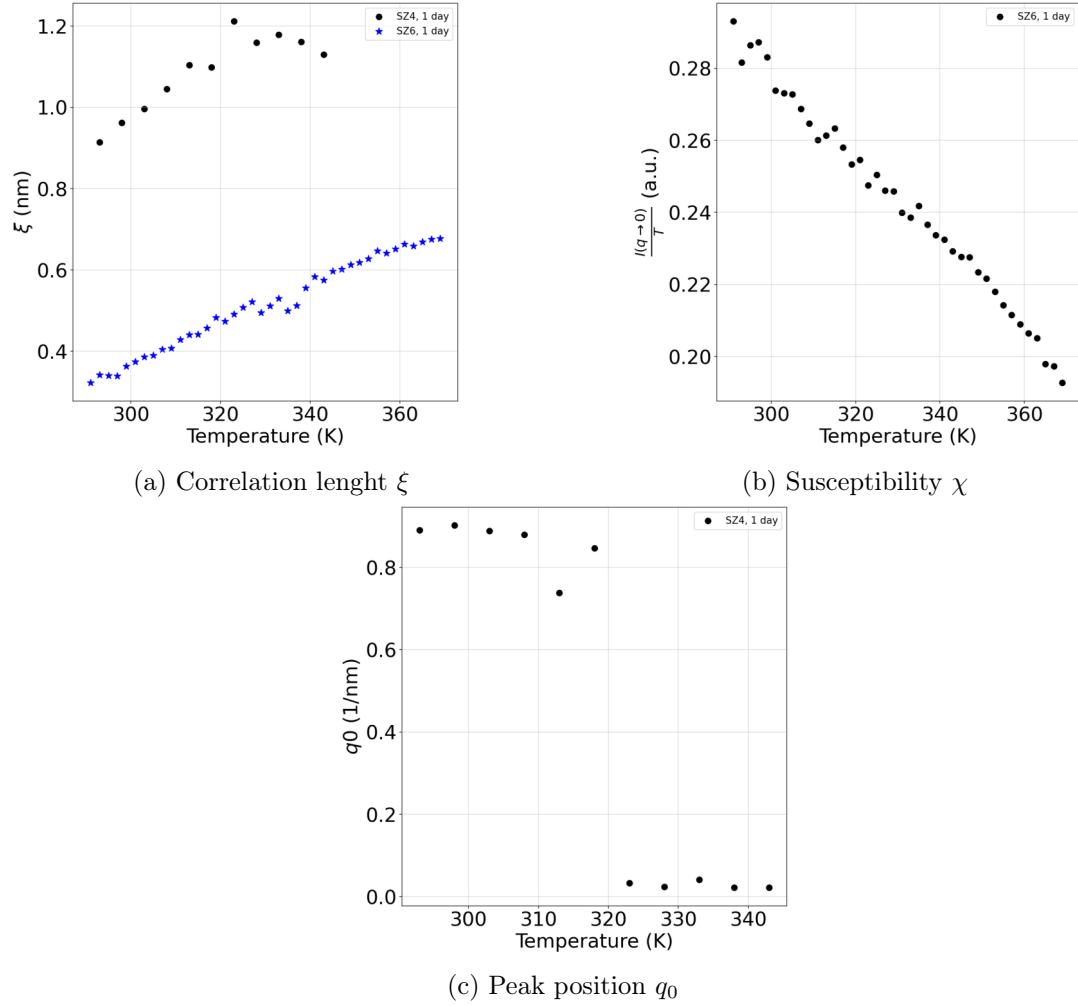


Figure 4.23.: (a) Correlation length ξ of SZ4 and SZ6
 (b) Susceptibility $I(q \rightarrow 0)/T$ as a function of temperature for sample SZ6
 (c) Peak position q_0 of SZ4.

4.4. HFIP-Water-Acid-Sodium Hydroxide

in the HFIP concnetration of both samples. The higher the HFIP concnetration, the lower the Scatt values are. On the other way around the higher the HFIP concnetration, the higher the Transmission values are. For SZ6, the Scatt values Figure 4.24a perform a small peak at around 330 K. The Trans values for SZ4 and SZ6 rising by the temperature.

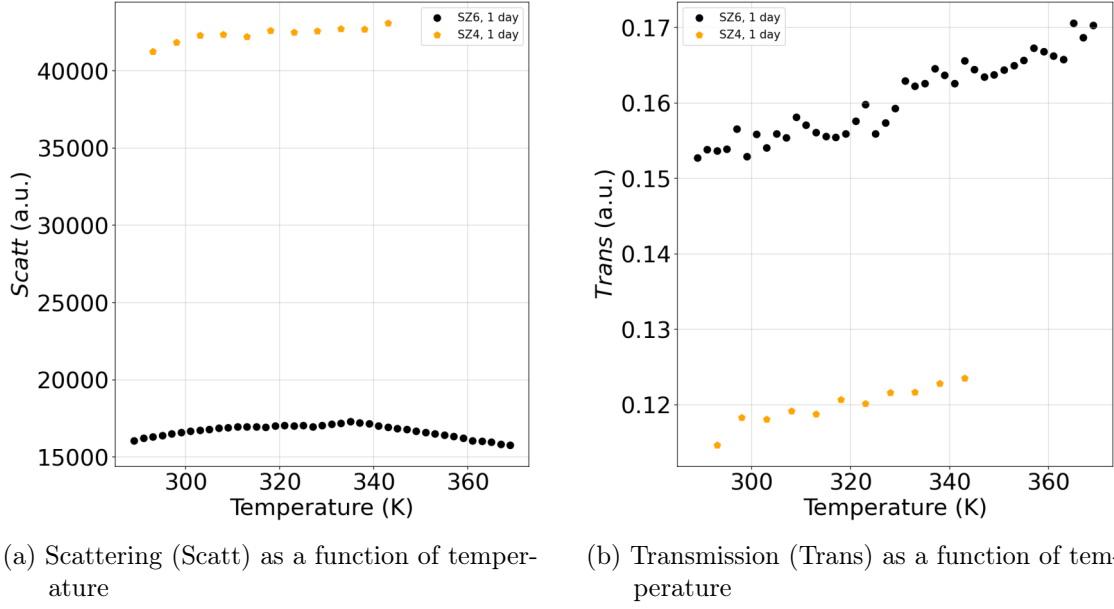


Figure 4.24.: a) Scattering intensity (Scatt) and (b) Transmission (Trans) as a function of temperature for samples SZ6 and SZ4.

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4.5. Water-Sodium Hydroxide

For comparability the sample SZ20 which includes just water and NaOH is analyzed. With these results one can compare the intensities of the samples including NaOH and see if there are artefacts that are coming from the NaOH. SZ20 contains $x_{\text{Water}} = 0.99973$ and $x_{\text{NaOH}} = 0.00027$ or in concentrations $c_{\text{NaOH}} = 0.02 \text{ molL}^{-1}$.

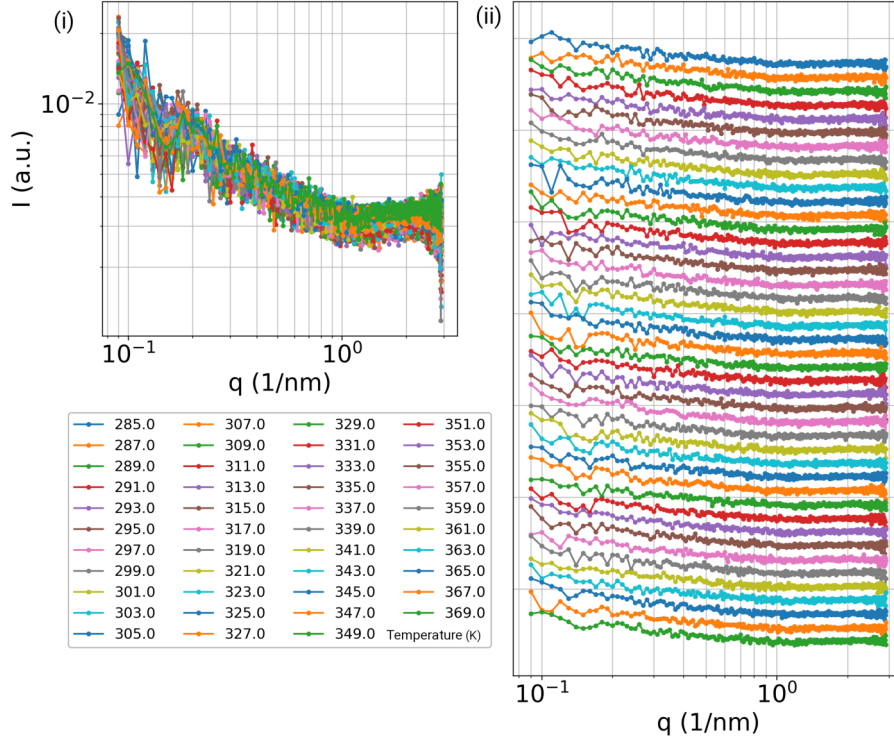


Figure 4.25.: Background corrected small-angle X-ray scattering (SAXS) intensity $I(q)$ as a function of the scattering vector q for a series of temperatures (in K) of the sample SZ20.

- (i) Data plotted on a logarithmic scale
- (ii) Waterfall representation of the same background-corrected data.

In total, the scattering signal of NaOH is relatively weak, about one order of magnitude lower compared to the HFIP-water mixtures. For sodium hydroxide in water, however, a pronounced increase in intensity is observed at small q . This feature was also found in several samples containing NaOH measured at room temperature, independent of whether they additionally included acid or only HFIP and water. Therefore, the low- q upturn can be directly attributed to the presence of NaOH in the mixtures. The strong increase at small q most likely results from the complete dissociation of NaOH into Na^+ and OH^- , leading to long-range concentration fluctuations in the solution.[2]

4.6. HFIP-Water-Antagonistic salt

The concept of adding antagonistic salts to HFIP–water mixtures is inspired by the study of such salts in water-solvent systems [5]. In that work, the presence of antagonistic salts caused the characteristic wave vector q_0 to shift away from zero. Motivated by these findings, two different antagonistic salts were introduced into HFIP-water mixtures at varying concentrations in the present study.

4.6.1. HFIP-Water-Tetraphenylposphonium chloride

In this section, three samples with different concentrations are analyzed. For all of them, the mole fraction of HFIP was kept constant in order to ensure reproducibility. Sample SZ13 contains $x_{\text{HFIP}} = 0.077$ and $x_{\text{TPhP}^+\text{Cl}^-} = 0.0013$, corresponding to a concentration of $c_{\text{TPhP}^+\text{Cl}^-} = 50 \text{ mmol L}^{-1}$. Thus, SZ13 contains a smaller amount of salt compared to the other two samples

Figure 4.26 displays three measurements of the same sample taken on different days. All measurements consistently show a peak around $q = 0.9 \text{ nm}^{-1}$. With increasing temperature, however, this peak shifts towards smaller q values. Such a shift is a clear indication of changes in the phase behavior of the mixture, likely reflecting an increase in characteristic length scales or the onset of structural reorganization within the system. The 2D image Figure 4.1c shows a concrete ring around the beamstop on the detector which als is an indication for this. For the analysis of the data, the Ornstein-Zernike model is not suitable due to the pronounced shift in the peak position. A double Gaussian function is also not appropriate, as it decays too rapidly at high q values, even though it reproduces the peak position reasonably well, Figure 4.27a. Similarly, the double Lorentzian model does not provide a satisfactory description: across the entire q -range the fit is inadequate, with clear deviations both at small and large q . At low q , the minimum cannot be captured properly by the two-Lorentzian form, while at high q the decay is too linear for this type of data, Figure 4.27b.

In contrast, the double Voigt profile describes the data very well. The additional curvature of the Voigt functions at high q values enables a much better fit compared to purely Gaussian or Lorentzian models. Furthermore, the Voigt model is robust against the peak shift and can also capture the minimum at small q values due to the flexibility of its functional form, Figure 4.27c. This indicates that the scattering pattern contains contributions that combine both Gaussian-like and Cauchy-Lorentzian-like features, which are naturally accounted for within the Voigt profile. However, sample SZ13 did not exhibit the expected phase behavior with both LCST and UCST transitions within a single measurement. To enhance the effect, the salt concentration was therefore increased to $c_{\text{TPhP}^+\text{Cl}^-} = 200 \text{ mmol L}^{-1}$. Figure 4.28 displays the corresponding intensity data for this mixture. The overall intensity remains on a comparable level to that observed for SZ13 and SZ7. With increasing salt concentration, however, the scattering ring in the 2D images becomes more pronounced, indicating stronger structural correlations in the system. SZ14 show the same behave as the sample SZ13. Just the peak is sharper in the inetnsity profil. Therefore also SZ14 is analyzed by the double voigt profil.

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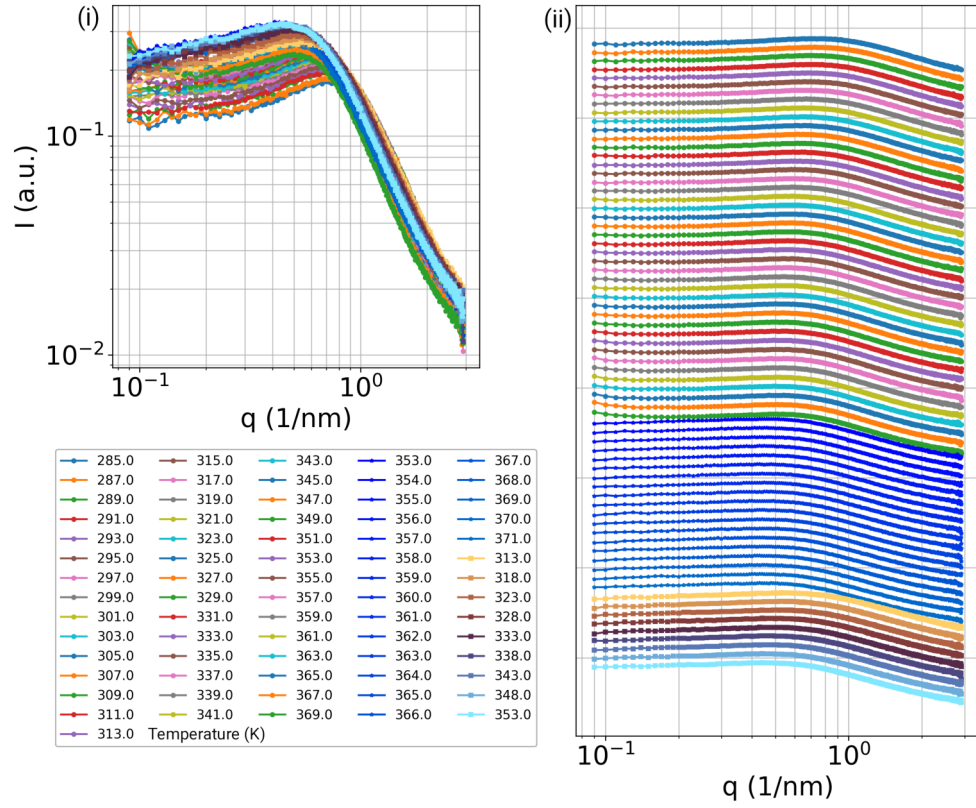
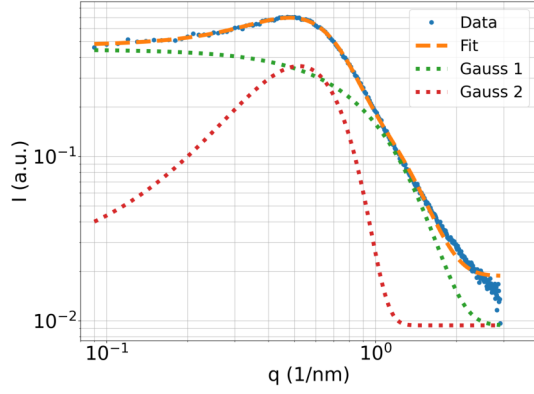


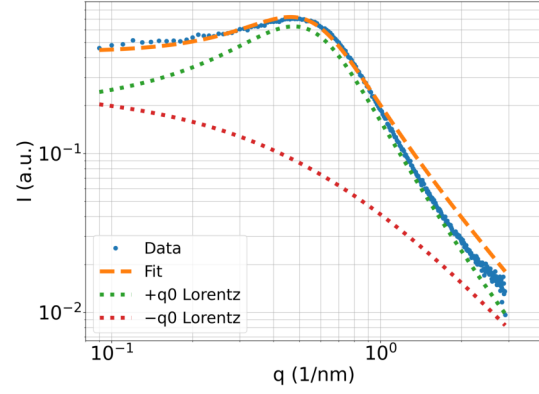
Figure 4.26.: Background corrected small-angle X-ray scattering (SAXS) intensity $I(q)$ as a function of the scattering vector q for a series of temperatures (in K) of the sample SZ13.

(i) Data plotted on a logarithmic scale

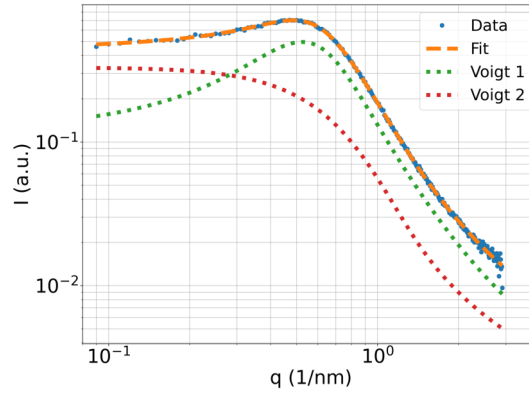
(ii) Waterfall representation of the same background-corrected data for clarity



(a) Double Gaussian



(b) Double Lorentzian



(c) Double Voigt

Figure 4.27.: Examples of different fitting models applied to the scattering data. (a) Double Gaussian fit with the individual Gaussian contributions. (b) Double Lorentzian fit with contributions at $\pm q_0$. (c) Double Voigt fit with the two Voigt contributions. The Voigt model reproduces the experimental data most accurately across the full q -range, capturing both the curvature at high q and the peak shift at lower q .

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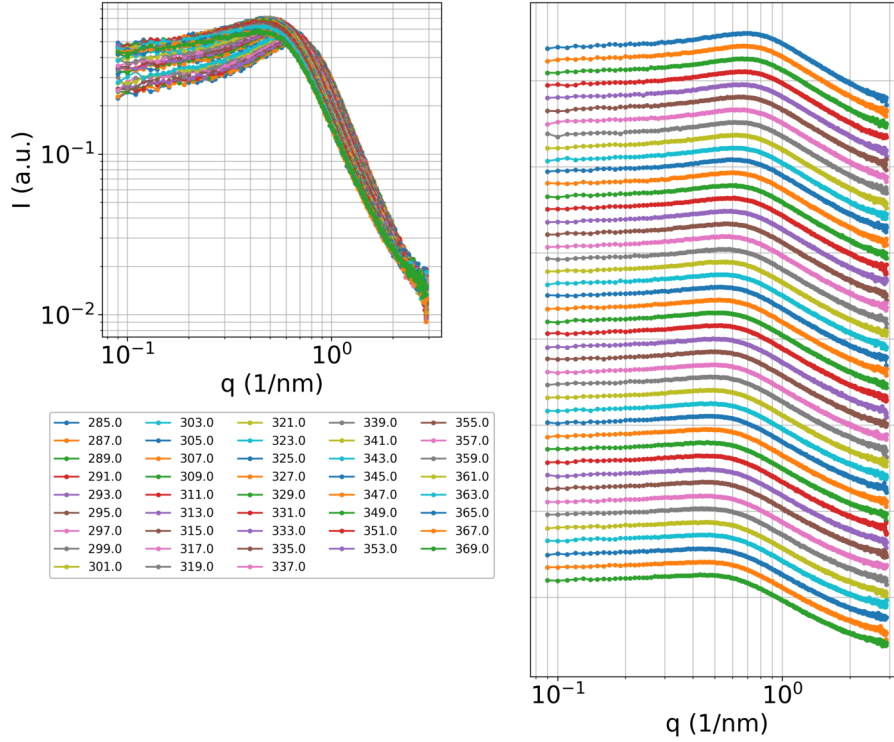


Figure 4.28.: Background corrected small-angle X-ray scattering (SAXS) intensity $I(q)$ as a function of the scattering vector q for a series of temperatures (in K) of the sample SZ14.
 (i) Data plotted on a logarithmic scale
 (ii) Waterfall representation of the same background-corrected data for clarity.

Again SZ14 did not show the expected behavior, another sample was produced with $c_{\text{TPHP}+\text{Cl}^-} = 400 \text{ mmol L}^{-1}$. While the production of this sample SZ18, the phase transition happens at room temperature and the mixture gets completely cloudy. This can be seen in subsection 4.7.3. Therefore, sample SZ19 was prepared with a salt concentration of $c_{\text{TPHP}+\text{Cl}^-} = 300 \text{ mmol L}^{-1}$. For this mixture, the intensity profile clearly reveals the presence of a LCST transition (Figure 4.29). During heating, the characteristic peak initially located at $q = 0.9 \text{ nm}^{-1}$ shifts continuously towards smaller q values until it eventually disappears at $q \approx 0 \text{ nm}^{-1}$. This behavior indicates a divergence of the characteristic length scale, which is a hallmark of critical phase separation near the LCST. The intensity is higher by a factor of 1 magnitude of order as SZ14. Once the peak vanishes, however, the data can no longer be adequately fitted with the applied models. The absence of a well-defined maximum makes it impossible to extract reliable structural parameters such as correlation length or susceptibility. In addition, the scattering becomes dominated by broad background contributions and long-range fluctuations, which further reduce the applicability of standard fitting functions. This suggests that in the vicinity of the LCST,

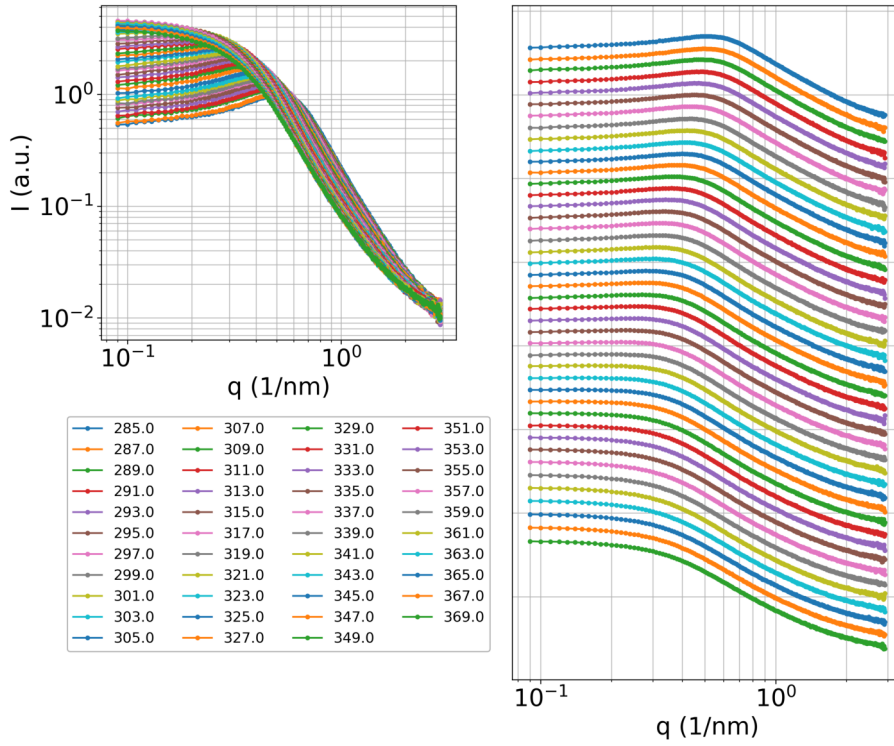


Figure 4.29.: Background corrected small-angle X-ray scattering (SAXS) intensity $I(q)$ as a function of the scattering vector q for a series of temperatures (in K) of the sample SZ19.

- (i) Data plotted on a logarithmic scale
- (ii) Waterfall representation of the same background-corrected data for clarity.

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the system enters a regime of strong critical fluctuations, where conventional models such as Lorentzian, Gaussian, or Voigt profiles are insufficient to capture the full complexity of the scattering signal. Eventhough the fit is executed for SZ19 with a double Voigt, but for temeratures higher than 350 K the correctness is not be given. This phase bevahior can be seen in subsection 4.7.3.

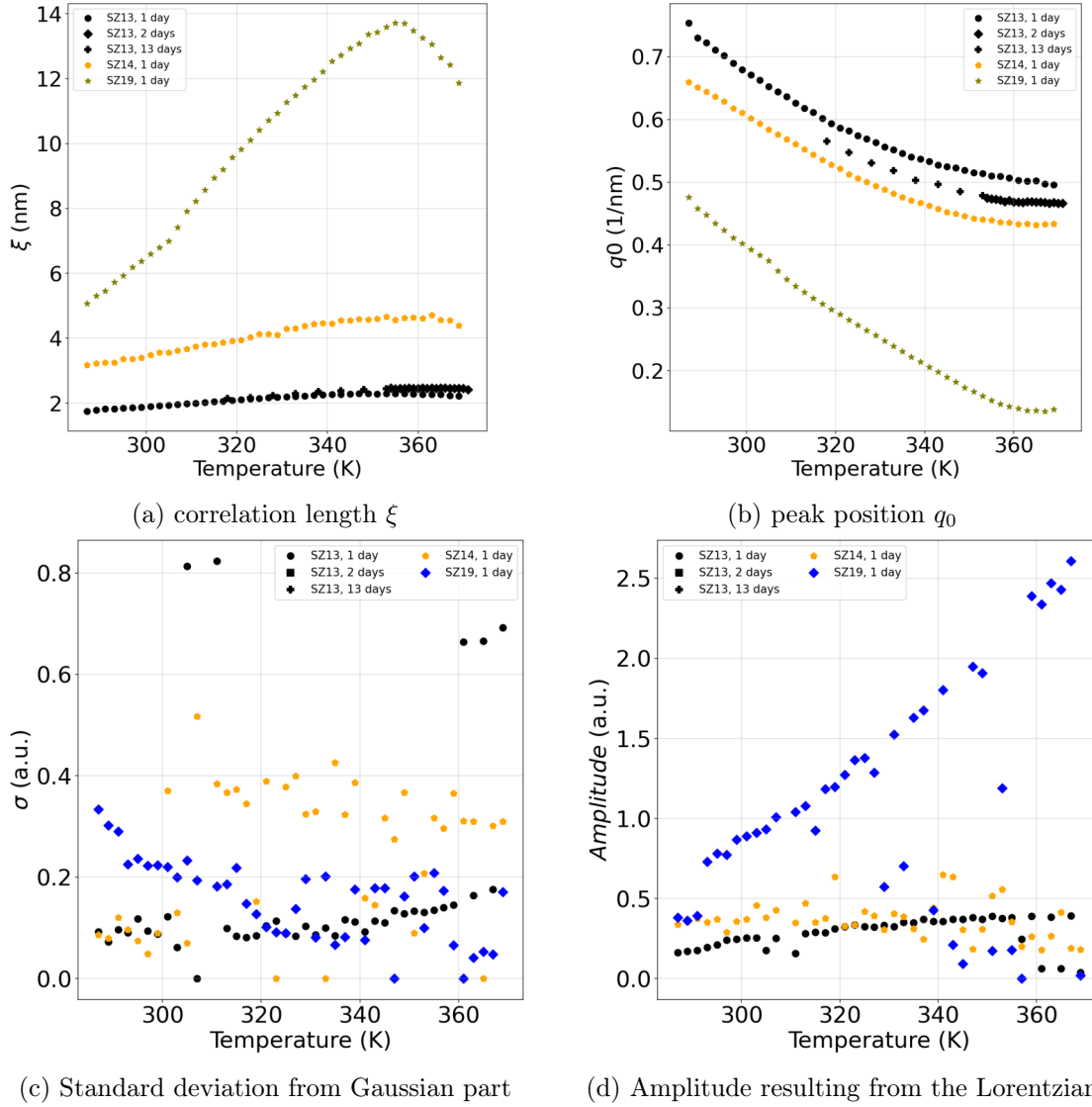


Figure 4.30.: Temperature dependence of (a) the correlation length ξ and (b) the peak position q_0 for different samples and sample ages. (c) Standard deviation from the Gaussian Part of the Voigt Model (d) Amplitude resulting from the Lorentzian Part of the Voigt Model While SZ13 and SZ14 show only moderate changes with increasing temperature, sample SZ19 exhibits a strong increase in ξ accompanied by a continuous shift of q_0 towards smaller values, eventually approaching zero. This behavior indicates the divergence of the characteristic length scale and is consistent with a LCST-type phase transition.

Figure 4.30 shows that the measurements of SZ13 taken on different days deviate from each other, yet follow the same overall trend. Moreover, the magnitude of ξ increases and

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of q_0 decreases with salt concentration. This observation is consistent with the intensity analysis, as both the shape of the peaks and their temperature-dependent shift support the same interpretation.

Figure 4.30 shows the temperature dependence of the Gaussian width σ and the Lorentzian amplitude. For the Gaussian contribution Figure 4.30c, SZ13 exhibits values close to zero for short storage times, but increases significantly after 13 days, indicating peak broadening. SZ14 remains at intermediate values with only weak temperature dependence, while SZ19 shows a decrease of σ with increasing temperature.

The Lorentzian amplitude Figure 4.30d is nearly constant and low for SZ13 and SZ14, whereas SZ19 displays a pronounced temperature dependence, increasing continuously up to values above 2.5.

Sample	SZ13, 1 day	SZ13, 2 days	SZ13, 13 days	SZ14	SZ19
γ	-	-	-	-	-
ν	0.57	0.57	0.50	0.70	2.04
δ	0.115	0.115	0.137	0.164	0.150

Table 4.5.: critical exponents resulting from the fitting process with Equation 2.23, Equation 2.24 and Equation 2.22 for SZ13, SZ14 and SZ19.

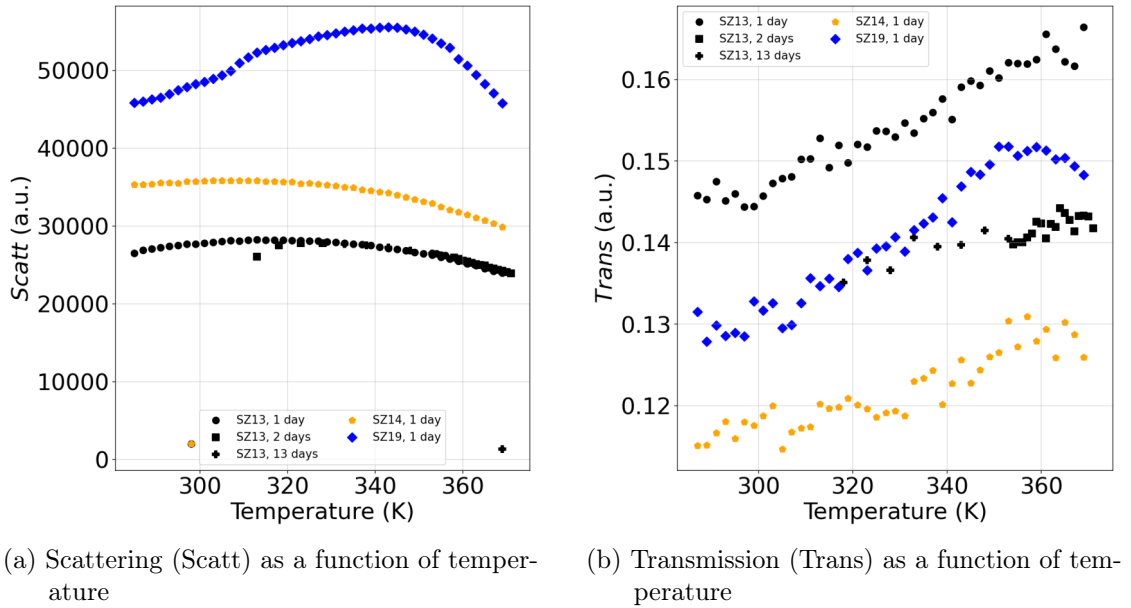


Figure 4.31.: (a) Scattering intensity (Scatt) as a function of temperature for SZ13, SZ14, and SZ19, including repeated measurements of SZ13 after 2 and 13 days. (b) Transmission (Trans) as a function of temperature for the same samples.

The scattering intensity increases with temperature and shows distinct maxima, with

SZ19 reaching the highest overall values. SZ14 lies in between, while SZ13 exhibits the lowest scattering signal. For SZ13, repeated measurements reveal a clear aging effect. after 13 days the intensity decreases significantly, indicating a reduction in structural correlations. The transmission increases gradually with temperature for all samples, with SZ13 showing the highest absolute values and SZ14 the lowest. The curves remain well separated, reflecting differences in sample composition and stability. Aging in SZ13 also leads to an increase in transmission, consistent with the reduced scattering observed in Figure 4.31a. In Addition the aging or vaporation effect can be seen in Figure 4.31b. The repeated measruemnts of SZ13 show a loss in Transmission, so the concentrationwithin the sample arised. The Trans plots of them are beyond the values of SZ19. By comparing the concentrations of salt, SZ19 includes the highest amount of salt. Then SZ14 follows and SZ13 includes the lowest amount of salt. Resulting from this, the order with in the Trans plot must be different. The values of SZ19 should be below them of SZ14 and SZ13. By comparing Figure 4.30a and Figure 4.31a, it can be seen, that the peak in ξ versus T for SZ19 is at the same position as the highest Scatt value in Figure 4.31a.

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4.6.2. HFIP-Water-Sodium Tetraphenylborate

In addition to TPhP^+Cl^- , the mirror salt NaBPh_4 was also used to prepare samples with the same concentrations as in the TPhP^+Cl^- -containing systems. Sample SZ16 contains the same amount of HFIP as the TPhP^+Cl^- samples, but with the mirror salt NaBPh_4 at a concentration of $c_{\text{NaBPh}_4} = 50 \text{ mmol L}^{-1}$. Figure 4.32 shows the analyzed data of SZ16.

At low temperatures, the scattering curves remain relatively flat, but upon heating to around 345 K a distinct peak emerges near $q = 0.4 \text{ nm}^{-1}$. With further increase in temperature, this peak shifts progressively to lower q values. Such behavior suggests that at sufficiently high temperatures a critical point could, in principle, be reached. However, this transition would occur above the boiling temperature of water and is therefore experimentally inaccessible.

Among the tested fitting functions, only the double Voigt model is able to describe the data adequately. This is due to the specific shape of the scattering curves: the Voigt profile combines Lorentzian- and Gaussian-like contributions, which allows it to reproduce both the curvature at high q and the peak shift at lower q , whereas pure Lorentzian or Gaussian models fail.

For the sample SZ17 with a salt concentration of $c = 200 \text{ mmol L}^{-1}$, the scattering intensity is shown in Figure 4.33. The overall intensity level is comparable to that of the samples with lower concentration, but the curves exhibit a more pronounced curvature in the intermediate q -range ($0.2\text{--}1 \text{ nm}^{-1}$). At small q values, the intensity increases only moderately without showing a strong upturn, while at higher q the decay follows a smooth, nearly power-law behavior. This suggests that the system develops enhanced structural correlations upon increasing the salt concentration, yet without clear evidence of a distinct peak or critical divergence at this concentration.

This particular concentration was also chosen in order to provide a direct comparison to the mirror salt NaBPh_4 , prepared at the same conditions. Such a comparison enables the influence of the counterion to be isolated, highlighting whether the observed scattering features arise from general ionic effects or from the specific chemical nature of TPhP^+Cl^- . With the same arguments SZ17 is only analyzable with the double Voigt profil. Both samples show in Figure 4.34 an increase in correlation length with rising temperature, accompanied by a shift of q_0 towards smaller values. While SZ16 exhibits a steady increase up to about 2.7 nm, SZ17 shows slightly lower values but follows a similar trend. After 10 days, the measurement of SZ17 reveals noticeable deviations, suggesting aging effects that influence both ξ and q_0 .

The standard deviation σ of the Gaussian component Figure 4.34c remains close to zero for sample SZ16 across the entire temperature range, indicating no significant temperature dependence. In contrast, SZ17 exhibits strongly increased σ values around 295 – 325 K, pointing to a pronounced peak broadening. At higher temperatures the values decrease again and approach zero. The amplitude of the Lorentzian component Figure 4.34d is initially small for SZ16 but increases continuously above about 340 K. For SZ17, the amplitudes are generally higher and show stronger fluctuations over the whole temperature range. In summary, SZ16 behaves rather stable with changes only at higher temperatures,

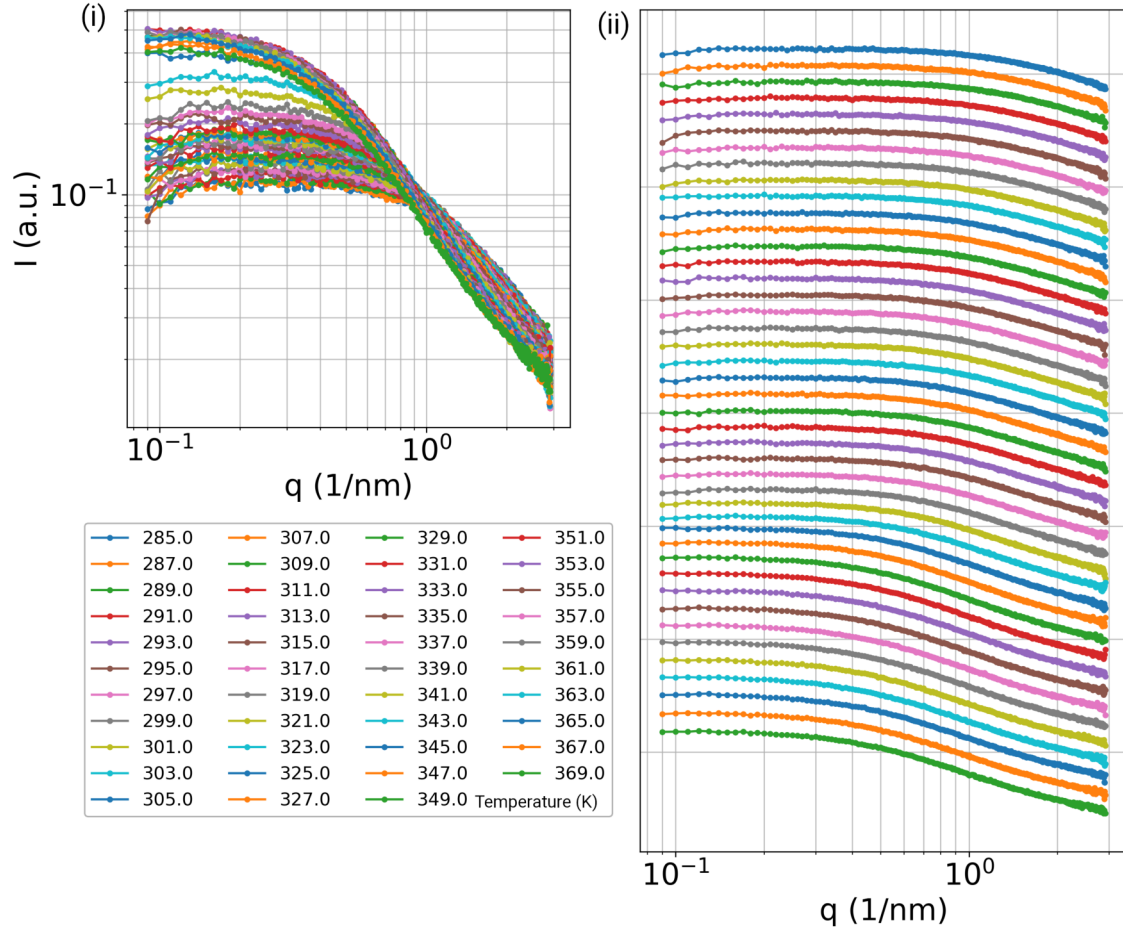


Figure 4.32.: Background corrected small-angle X-ray scattering (SAXS) intensity $I(q)$ as a function of the scattering vector q for a series of temperatures (in K) of the sample SZ16.

(i) Data plotted on a logarithmic scale.

(ii) Waterfall representation of the same background-corrected data.

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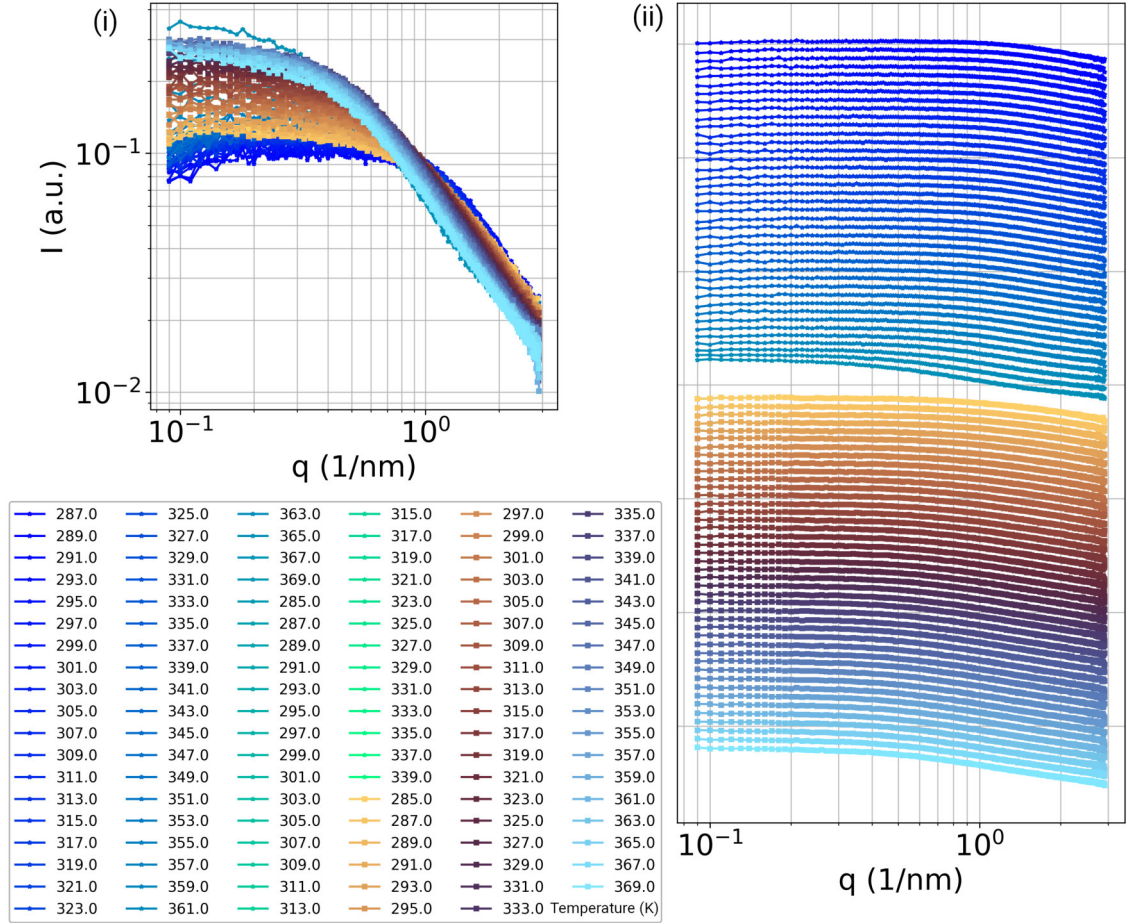


Figure 4.33.: Background corrected small-angle X-ray scattering (SAXS) intensity $I(q)$ as a function of the scattering vector q for a series of temperatures (in K) of the sample SZ17.

(i) Data plotted on a logarithmic scale.

(ii) Waterfall representation of the same background-corrected data.

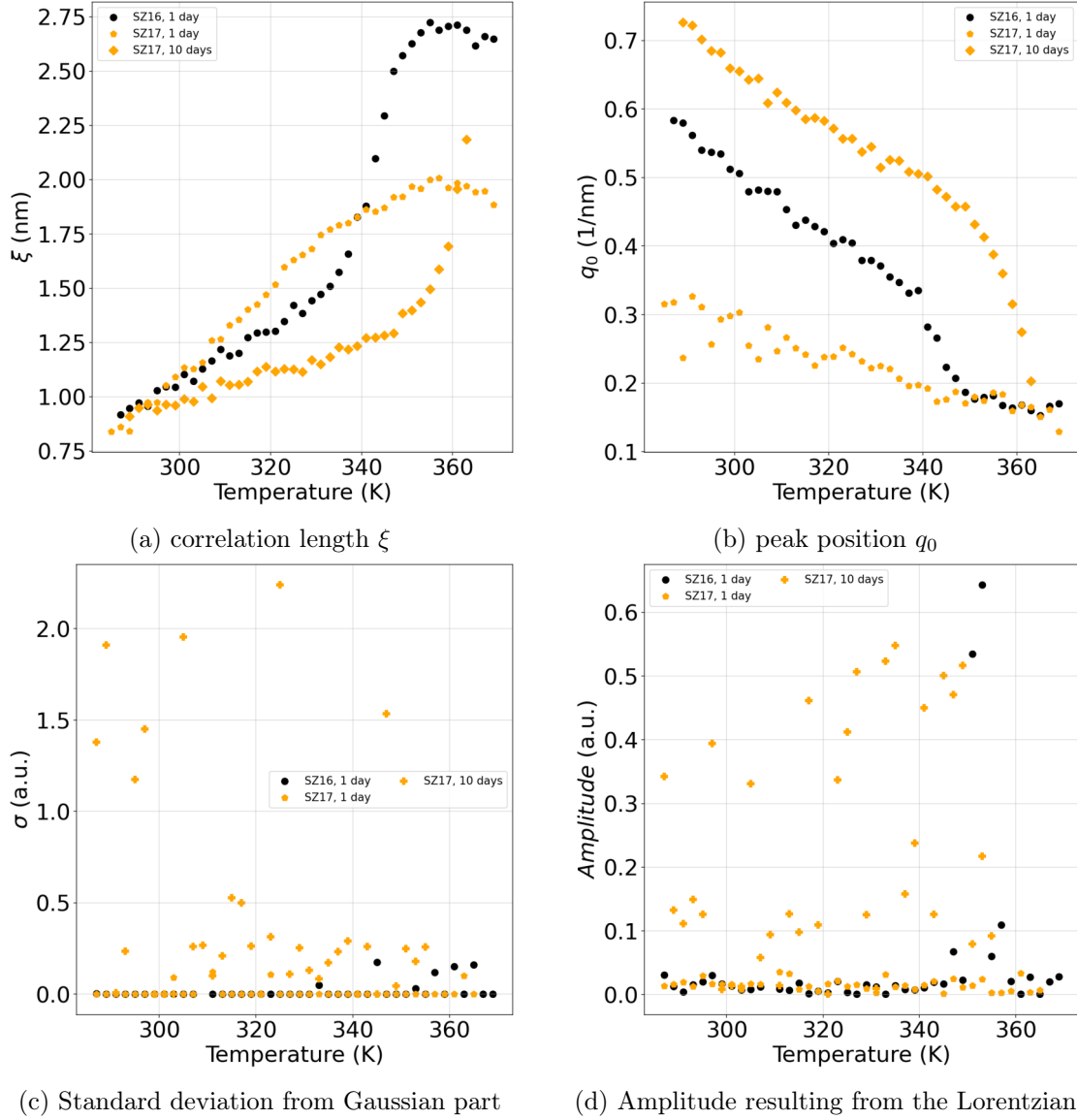


Figure 4.34.: Temperature dependence of (a) the correlation length ξ and (b) the peak position q_0 for samples SZ16 and SZ17. (c) Standard deviation from the Gaussian Part of the Voigt Model (d) Amplitude resulting from the Lorentzian Part of the Voigt Model

4. Results

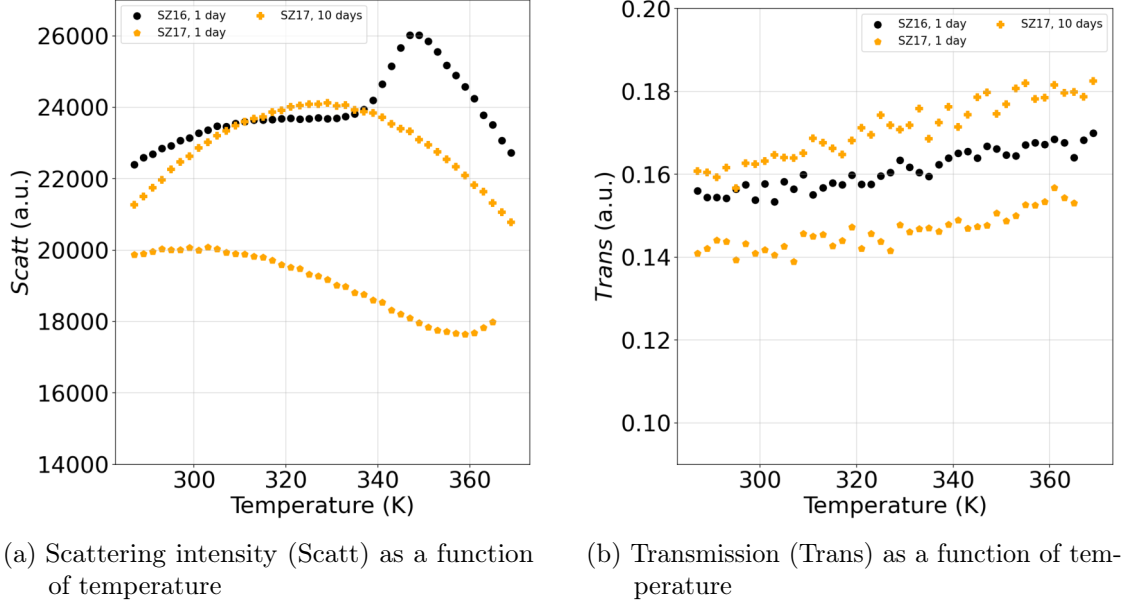


Figure 4.35.: a) Scattering intensity (Scatt) as a function of temperature for samples SZ17 (1 and 10 days) and SZ16.
(b) Transmission (Trans) as a function of temperature for the same samples.

while SZ17 already shows clear deviations at lower temperatures. The repeated measurement of SZ17 after 10 days, however, reveals a markedly different behavior: the correlation length decreases significantly, and the overall progression of ξ deviates strongly from the initial measurement. This rapid aging effect indicates that the microstructure of SZ17 changes much faster compared to SZ16. In addition, the evolution of q_0 for SZ17 does not follow a simple concentration dependent trend, suggesting that the peak position cannot be directly related to the salt concentration in this case, but is instead strongly influenced by aging and time dependent structural rearrangements.

Sample	SZ16, 1 day	SZ17, 1 day	SZ17, 10 days
γ	-	-	-
ν	0.99	-	2.47
δ	0.067	-	0.204

Table 4.6.: critical exponents resulting from the fitting process with Equation 2.23, Equation 2.24 and Equation 2.22 for SZ16 and SZ17.

Due to the data, an estimation for SZ17 (1 day) was not possible. Therefore – marks this missing values. The scattering curves show clear differences between SZ17 and SZ16. For SZ16, a maximum around 345 K is observed, consistent with critical fluctuations near

the LCST. In contrast, SZ17 exhibits a steady decrease in intensity with temperature, and after 10 days the curve flattens further, highlighting strong aging effects that suppress the scattering signal. The transmission increases gradually with temperature for all samples. SZ17 shows a shift upon aging, reaching higher transmission values after 10 days, which corresponds to a reduced scattering intensity. SZ16, however, remains more stable, with only small changes over the measured temperature range.

Figure 4.35a shows the scattering intensity (*Scatt*) as a function of temperature for SZ17 and SZ16. For SZ17 (1 day), the intensity initially increases slightly with temperature and then levels off, while for SZ17 (10 days) a decrease is observed above approximately 320 K, indicating structural changes upon aging. In contrast, SZ16 (1 day) exhibits a continuous rise of the scattering intensity up to around 350 K, followed by a drop at higher temperatures. This behavior suggests differences in the underlying microstructure and thermal stability between the samples.

Figure 4.35b depicts the corresponding transmission (*Trans*). All samples show a general increase with temperature, which can be attributed to reduced scattering at elevated thermal energy. SZ17 (10 days) maintains a higher transmission compared to the prepared SZ17 (1 day), consistent with the reduced scattering intensity. SZ16 (1 day) lies between these two cases, showing intermediate scattering and transmission. The aging effect for SZ17 leads to a weakening of scattering and enhancement of transmission. The differences in concentrations of SZ16 and SZ17 are indicating the differences in the *Scatt* and *Trans* plots. For the higher Concentration of the salt, so for SZ17, the *Scatt* is lower than for SZ16. Eventhpugh due to the aging effect, the SZ17 measuremnt after 10 days is crossing the *Scatt* plot of SZ16 around 300 K. This indicates, that the aging effect or the measurments are actually affecting the composition within the samples. an analog behavior can be seen in Figure 4.35b, but here no crossing behavior exists.

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4.7. Supplemental Sample Characterization

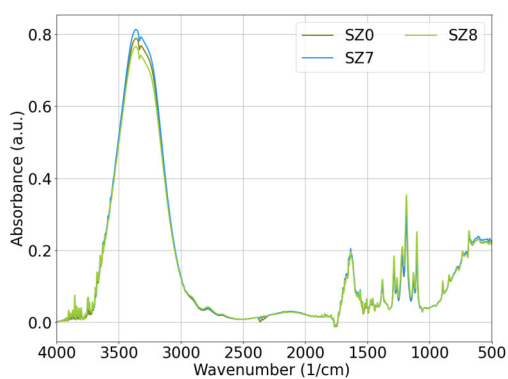
In addition to the SAXS investigations, some complementary measurements were performed in order to obtain a more comprehensive understanding of the studied systems. These additional analyses include attenuated total reflectance (ATR) spectroscopy to characterize the chemical composition of the samples, pH measurements to evaluate the acidity and its variation with composition, as well as optical observations of the samples during heating and cooling to visualize macroscopic changes in appearance. Furthermore, background measurements were carried out to ensure proper data correction and reliable interpretation of the scattering results.

4.7.1. Attenuated Total Reflectance

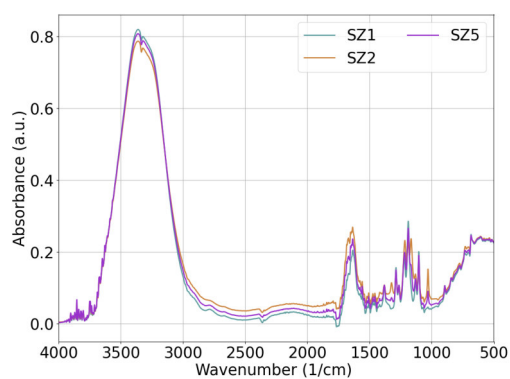
The attenuated total reflectance (ATR) measurements were performed to characterize the chemical composition of the mixtures and to probe possible changes in molecular interactions. In particular, ATR provides insights into the formation or modification of hydrogen-bonding networks that may occur when mixing the different constituents. The evaluation was carried out qualitatively, focusing on identifying characteristic differences between samples with different compositions rather than extracting quantitative parameters.

Figure 4.36a shows the ATR spectra of the HFIP-water samples SZ0, SZ7, and SZ8, which differ only in their HFIP concentration. Specifically, the HFIP concentrations are $c_{\text{HFIP}} = 3.10 \text{ mmol L}^{-1}$ for SZ0, 3.14 mmol L^{-1} for SZ7, and 2.75 mmol L^{-1} for SZ8. By comparing these data with the spectra of pure water and pure HFIP, the broad absorption band centered around 3400 cm^{-1} is assigned to the O–H stretching vibration of water, while the bands in the region $1000 - 1750 \text{ cm}^{-1}$ can be attributed to characteristic HFIP vibrations, including C–F and C–O stretching modes. The intensity of the C–O stretching band around 3400 cm^{-1} increases slightly with increasing HFIP concentration, which is consistent with enhanced hydrogen bonding and possible changes in the solvent structure. The sample SZ7, with the highest HFIP concentration, exhibits the most intense O–H band. In contrast, SZ8 shows a slightly lower absorbance, consistent with its lower HFIP content. Interestingly, the spectral region between $1000 - 1500 \text{ cm}^{-1}$ shows an inverse trend, here, the sample with the lowest HFIP concentration (SZ8) exhibits the highest absorbance. This may be due to reduced overlap or cancellation between HFIP and water bands, as well as more pronounced individual HFIP contributions at lower concentrations. By contrast, in the ranges $1500 - 1750 \text{ cm}^{-1}$ and $500 - 1000 \text{ cm}^{-1}$, the spectra of SZ0 and SZ7, the samples with the highest HFIP content, show slightly stronger absorption features, indicating concentration dependent enhancement of specific HFIP vibrations in these regions. Figure 4.36b presents the ATR spectra of samples containing water, HFIP, and pentafluoropropionic acid at varying concentrations. Sample SZ1, with $c_{\text{HFIP}} = 3.1 \text{ mmol L}^{-1}$, $c_{\text{acid}} = 0.063 \text{ mmol L}^{-1}$, and $c_{\text{water}} = 36.48 \text{ mmol L}^{-1}$, contains only a very small amount of pentafluoropropionic acid. Accordingly, its spectrum closely resembles that of the corresponding HFIP-water sample SZ0 (Figure 4.36a). Nevertheless, closer inspection reveals that the absorption band in the region $1500 - 1750 \text{ cm}^{-1}$ is

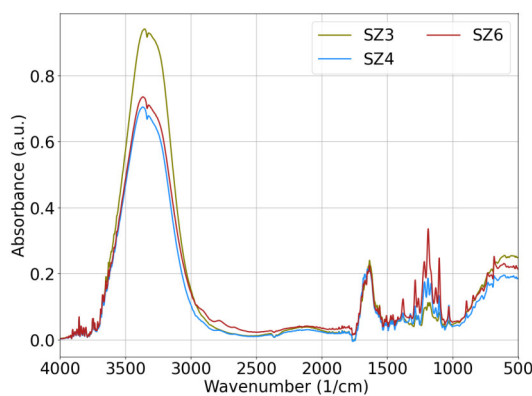
4.7. Supplemental Sample Characterization



(a) HFIP-Water samples



(b) HFIP-Water-Pentafluoropropionic Acid samples



(c) HFIP-Water-Pentafluoropropionic Acid-NaOH samples

Figure 4.36.: Attenuated total reflectance (ATR) measurement data of selected samples. The plotted spectra are grouped according to the components of the mixtures.

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significantly more pronounced compared to the acid-free samples. This enhancement can be attributed to the spectrum of pure pentafluoropropionic acid, which shows a strong absorption band at exactly this position. At the same time, the characteristic HFIP band decreases in intensity relative to the HFIP-water spectrum in Figure 4.36a. For sample SZ2, the concentration of HFIP was decreased to $c_{\text{HFIP}} = 1.68 \text{ mmol L}^{-1}$, and on the other hand, the concentration of the acid was increased to $c_{\text{acid}} = 0.67 \text{ mmol L}^{-1}$. With this composition, SZ2 contains the highest concentration of acid among the samples. Its spectrum exhibits the lowest absorption in the O–H stretching region around $3000 - 3500 \text{ cm}^{-1}$, while the band in the carbonyl region $1500 - 1750 \text{ cm}^{-1}$ is the most intense. For sample SZ5, the HFIP concentration was increased again to $c_{\text{HFIP}} = 2.99 \text{ mmol L}^{-1}$, while the acid concentration was reduced to $c_{\text{acid}} = 0.387 \text{ mmol L}^{-1}$. This adjustment of HFIP was made due to the statement, that HFIP-Water mixtures have the highest intensities with $x_{\text{HFIP}} = 0.077$.^[47] So SZ5 and SZ1 contain $x_{\text{HFIP}} = 0.07705$ while SZ2 only contains $x_{\text{HFIP}} = 0.039$. Interestingly, the spectral differences between SZ5 and the other samples are less pronounced, the absorption in the O–H stretching region $3000 - 3500 \text{ cm}^{-1}$ increases again compared to SZ2, and the intensity of the carbonyl band around 1680 cm^{-1} decreases slightly. The absorbance maximum of the O–H stretching band is approximately 0.82 for SZ1 and decreases to about 0.81 for SZ5 and 0.76 for SZ2, reflecting reduced hydrogen bonding due to the increased acid content. Simultaneously, the peak height at 1680 cm^{-1} , associated with the C=O stretching vibration of pentafluoropropionic acid, increases from SZ1 over SZ5 up to SZ2. This trend correlates well with the rising concentration of pentafluoropropionic acid and matches the position of the main absorption in the spectrum of the pure acid. Additionally, slight broadening of the carbonyl band is observed for SZ2, likely due to changes in the hydrogen-bonding environment. The spectral region between $1750 - 3000 \text{ cm}^{-1}$ also reveals increasing divergence between the spectra, possibly caused by combination bands or overlapping vibrational modes related to acid-HFIP interactions.

Figure 4.36c contains spectra of three samples including HFIP, water, Pentafluoropropionic acid and Sodium Hydroxid. The varying in HFIP, Acid and NaOH concentrations. Sample SZ3 contains equimolar amounts of NaOH and acid ($c_{\text{NaOH}} = 0.45 \text{ mmol L}^{-1}$, $c_{\text{acid}} = 0.45 \text{ mmol L}^{-1}$), and $c_{\text{HFIP}} = 0.86 \text{ mmol L}^{-1}$, thus representing a fully neutralized system with a moderate HFIP content. The spectrum of SZ3 shows a strongly reduced C=O absorption band at 1680 cm^{-1} compared to the un-neutralized sample SZ2, consistent with the conversion of the acid to its carboxylate form, which typically absorbs at lower frequencies or displays broader signals.^[2] At the same time, the O–H stretching band in the range $3000 - 3500 \text{ cm}^{-1}$ regains intensity, suggesting the reestablishment of hydrogen bonding via hydroxide or HFIP-carboxylate interactions. Sample SZ4 features a higher content of all three components ($c_{\text{NaOH}} = 0.878 \text{ mmol L}^{-1}$, $c_{\text{HFIP}} = 1.885 \text{ mmol L}^{-1}$, $c_{\text{acid}} = 0.743 \text{ mmol L}^{-1}$), thus remaining slightly base rich. The corresponding spectrum shows a further suppression of the carbonyl band, while the O–H band remains broad and relatively intense. This indicates the presence of both water-HFIP and HFIP-carboxylate hydrogen bonding networks. In contrast, sample SZ6 has the highest HFIP concentration ($c_{\text{HFIP}} = 2.96 \text{ mmol L}^{-1}$), with

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lower base and acid content ($c_{\text{NaOH}} = 0.3718 \text{ mmol L}^{-1}$, $c_{\text{acid}} = 0.3849 \text{ mmol L}^{-1}$), leading to a near-neutral 1 : 1 salt formation at high HFIP background. In this spectrum, the C=O absorption is nearly absent, and the broad O–H stretching region dominates. Compared to SZ3 and SZ4, the spectrum of SZ6 reflects a more homogeneous HFIP-rich environment with less spectral contribution from protonated or hydrogen-bonded carboxylic acid. The interpretation that the disappearance of the C=O band upon NaOH addition is a clear indication of acid neutralization. Simultaneously, the shape and intensity of the O–H stretching band depend on the total HFIP content and the balance between hydrogen bonding and ion pairing in the mixture.

All spectra exhibit a pronounced dip at approximately 2400 cm^{-1} , resulting from the asymmetric stretching vibration of atmospheric CO_2 . This feature is an artifact in ATR spectra and should be disregarded in the interpretation.

4.7.2. pH Values

The pH values of all prepared samples were measured using commercial indicator test strips. This approach allows for a rapid screening of the acidity and basicity of the solutions and serves as a straightforward verification of the expected chemical conditions. The pH of HFIP-water mixtures is a crucial factor, as it directly affects ionization equilibria, hydrogen bonding, and thereby the formation of microheterogeneities. Figure 4.37 gives an overview of the pH values of the produced samples. The pH value of pure HFIP in aqueous solution is typically in the range of 3-4, confirming its acidic character.[29]

When water is added to HFIP, the pH value of the resulting mixture increases compared to the pure substance. This effect arises because the dissociation of HFIP in aqueous solution leads to a reduction in proton concentration upon dilution with water. Consequently, the molarity of H^+ ions decreases, which in turn results in an increase of the pH value according to the relation given in the corresponding equation.

$$pH = -\log [\text{H}^+] \quad (4.7)$$

Here, $[\text{H}^+]$ denotes the molarity of hydrogen ions. Accordingly, increasing the proportion of water in the mixture leads to a higher pH value.[2] The measured pH values of the HFIP-water samples lie between 5 and 6, as shown for samples SZ0 and SZ7–SZ11 in Figure 4.37. In contrast, the samples containing different concentrations of pentafluoropropanoic acid (SZ1, SZ2 and SZ5) exhibit pH values in the range of 0 to 3, which is consistent with expectations for acidic components at such concentrations. Due to the strong acidity of pentafluoropropanoic acid, as summarized in Table A.2, the proton concentration significantly exceeds that of the HFIP-water mixtures alone. As a result, the molarity of H^+ ions increases, which directly lowers the pH value according to Equation 4.7.

4. Results

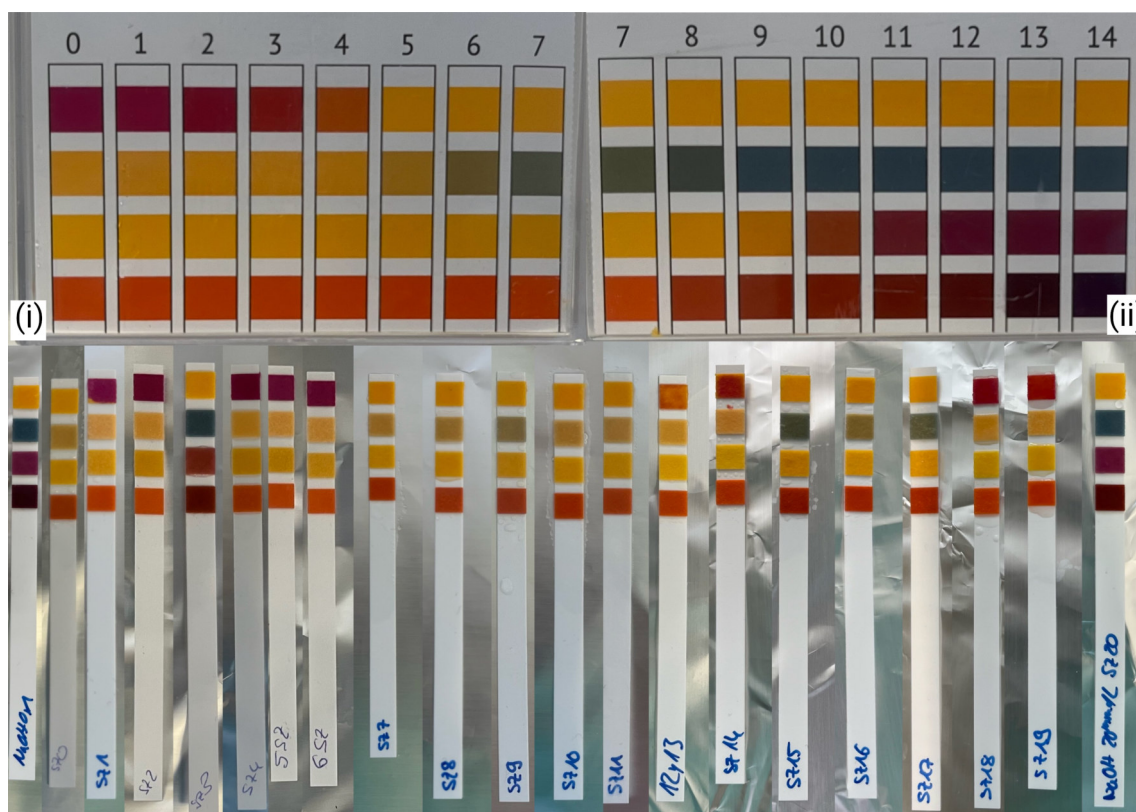


Figure 4.37.: pH determination of all prepared samples using test strips. Panels (i) and (ii) show the corresponding reference color charts.

For one of the samples containing both NaOH and pentafluoropropionic acid (SZ3), the measured pH value increased to 10, which is consistent with the expected behavior after the addition of a strong base. In contrast, for the other two samples containing both the acid and NaOH (SZ4 and SZ6), the pH value dropped back to 0. One possible explanation is that the amount of NaOH was insufficient, leading to incomplete neutralization of the acid and thus maintaining a strongly acidic environment. Another possibility is that the acid forms clusters or aggregates in the mixture. Upon addition of NaOH, these aggregates may be disrupted, releasing additional protons into the solution. As a result, the pH decreases despite the presence of NaOH in the sample.[2]

Additionally, the sample containing HFIP-water-NaOH (SZ15) exhibited a pH value of approximately 7, indicating that the solution was neutralized. This increase in pH results from the addition of a sufficient concentration of a strong base to an initially acidic solution. Accordingly, the concentration of NaOH must be high enough to achieve complete neutralization.[2]

The first test strip, see Figure 4.37, corresponds to a 1 mol L^{-1} NaOH solution, for which a pH value of 14 was measured, in good agreement with the literature value. In contrast, the last test strip in Figure 4.37 corresponds to a 20 mmol L^{-1} NaOH solution, which

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yielded a pH value of 12, also consistent with literature data. As expected, the lower concentration of NaOH results in a reduced pH value.[2]

For salt solutions, the resulting pH value depends on the acidic or basic character of the constituent ions. If the anion is not the conjugate base of a weak acid, it will be neither acidic nor basic, and thus the cation must be considered. In this case, the cation may either be an acidic metal ion or the conjugate acid of a weak base. If one ion in the salt acts as an acid and the other as a base, both contribute to determining the overall pH value of the solution.[2]

For the samples SZ12-14 and SZ18-19, different concentrations of tetraphenylphosphonium chloride were dissolved in HFIP-water mixtures of fixed composition. The anion of this salt is Cl^- , which has a neutral character as the conjugate base of a strong acid. [2] Consequently, the cation, tetraphenylphosphonium $(\text{C}_6\text{H}_5)_4\text{P}^+$, must be considered. This cation is also regarded as chemically neutral, since its charge is stabilized by the four phenyl groups (see skeletal formula in Figure 3.10b). Therefore, the salt as a whole behaves essentially neutrally in solution. As a result, the addition of tetraphenylphosphonium chloride does not significantly alter the pH of the HFIP-water mixtures compared to the reference sample. The measured pH values of these samples are between 3 and 4, as shown in Figure 4.37. In comparison, the base mixture SZ7 (HFIP-water without salt) shows a pH of 4, demonstrating that the influence of this antagonistic salt on the acidity is, as expected from theory, rather small. Nevertheless, at higher concentrations of tetraphenylphosphonium chloride (300 mmol L^{-1} and 400 mmol L^{-1}), the pH decreases slightly to a value of 3.

A corresponding analysis can be carried out for the antagonistic salt sodium tetraphenylborate, which was investigated in samples SZ16 and SZ17 at concentrations of 50 mmol L^{-1} and 200 mmol L^{-1} , respectively. The anion tetraphenylborate $(\text{C}_6\text{H}_5)_4\text{B}^-$ is considered chemically neutral, as it represents the conjugate base of a strong acid, analogous to the cation tetraphenylphosphonium $(\text{C}_6\text{H}_5)_4\text{P}^+$. The skeletal formula of sodium tetraphenylborate is shown in Figure 3.11b. The cation Na^+ , being a group 1 metal ion, is also neutral.[2] Therefore, the addition of sodium tetraphenylborate is not expected to significantly change the pH of HFIP-water mixtures compared to the reference system. Experimentally, however, the measured pH values for these samples were found to increase to 6 and 7. One possible explanation is that the addition of salt increases the ionic strength of the solution, which suppresses the dissociation of HFIP. As a consequence, fewer H^+ ions remain free in solution, leading to a higher pH value. Additionally, the hydrophobic character of the tetraphenylborate anion may facilitate specific interactions with HFIP, further reducing the effective proton concentration. Thus, sodium tetraphenylborate indirectly influences the pH not by direct acid-base chemistry, but through structural effects on the solvent environment and ion-solvent interactions.

4.7.3. Images

For visual confirmation and to determine the range within the critical temperature of the phase transition, the samples containing antagonistic salts were subjected to a cooling and heating cycle. Cooling was performed by placing the samples in a freezer for 5

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minutes. Subsequently, reheating was carried out in a water bath positioned on a heating plate, into which the samples were immersed. After the cooling step, the samples were illuminated with a lamp to observe whether turbidity appeared. Once the samples are approximately handwarm, they were transferred to the water bath for controlled heating. At regular time intervals, the samples were inspected under the lamp. In general, prior to the transition from clear to fully turbid, faint streak-like turbidity could already be observed in some samples.

Figure 4.38 illustrates the most clearly observable phase transitions. The temperature increases stepwise from image (i) to image (v). It can be seen that the sample passes through two distinct turbidity states at different temperatures, corresponding to a lower and an upper critical solution temperature (LCST and UCST). The first turbidity state appears immediately after removal from the freezer, as shown in Figure 4.38 (i). This marks the LCST, where phase separation occurs upon heating from low temperature. With increasing temperature, the turbidity gradually decreases, and the sample becomes fully transparent at approximately hand-warm temperature, as depicted in Figure 4.38 (iii). Upon further heating in the water bath, faint streak-like turbidity reappears at around 50 °C, although this state could not be photographed. At higher temperatures, the sample again shows pronounced turbidity, visible in Figure 4.38 (iv), until complete turbidity is reached at about 80 °C, as shown in Figure 4.38 (v). This second transition corresponds to the UCST, where phase separation occurs upon heating beyond a critical temperature. The mixture, mentioned in Figure 4.38, is the only sample in which both phase transitions (LCST and UCST) could be observed under this type of heating and cooling procedure.

In addition, phase separation was clearly visible to the naked eye, although the photographs do not capture this effect satisfactorily. Furthermore, the solutions appeared to become more viscous during the formation of the streak-like turbidity.

Figure 4.39 illustrates an observable lower phase transition. The temperature increases stepwise from image (i) to image (iii), during which the system passes through turbidity states at low temperature, corresponding to a lower critical solution temperature (LCST). Immediately after removal from the freezer, the sample exhibits streak-like turbidity, as shown in Figure 4.39 (i). When left at room temperature (20 °C), the turbidity gradually increases, which is visible in Figure 4.39 (ii). At this point, the sample becomes fully turbid, as depicted in Figure 4.39 (iii). Once the sample equilibrates to room temperature, it remains completely turbid, thus confirming the presence of a lower critical solution temperature. By reaching higher temperatures, the sample gets completely clear again. Unfortunately an upper critical solution temperature could not be reached for this sample with this method. But by comparing the images with the analyzed SAXS data, one can see that there exists an upper critical solution temperature, at over 70 °C.

Figure 4.40 illustrates an beginning turbidity. The temperature increases stepwise from image (i) to image (iii), during which the system passes through turbidity states at low temperature. Immediately after removal from the freezer, the sample remains clear, as shown in Figure 4.40 (i). Upon equilibration at room temperature (20 °C), turbidity develops, which can be seen in Figure 4.40 (ii). After subsequent heating, the sample

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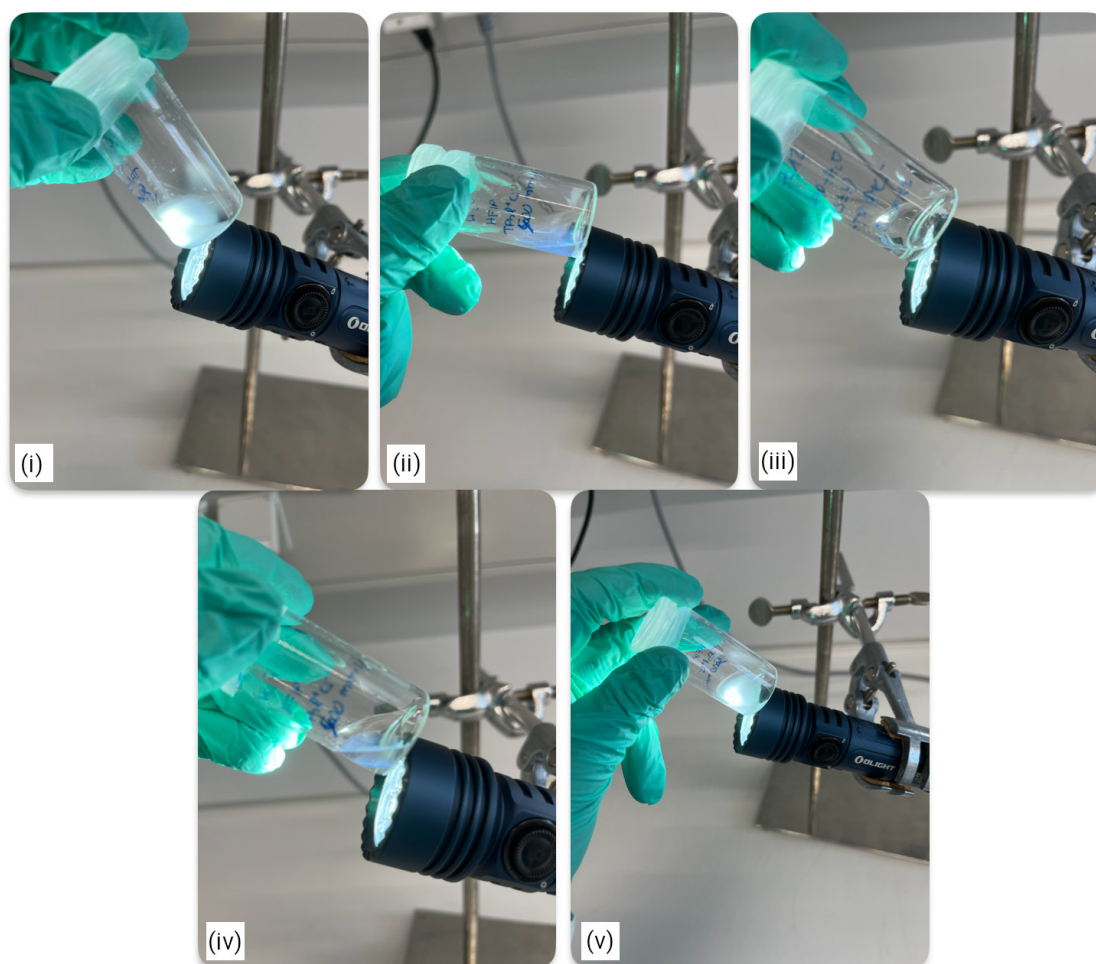


Figure 4.38.: Images of the sample containing 3.15 mmol L^{-1} of HFIP, $37.17 \text{ mmol L}^{-1}$ of water and 400 mmol L^{-1} of TPhP^+Cl^- . The temperature was varied from low in image (i) to high in image (v), showing both the lower and upper phase transitions.

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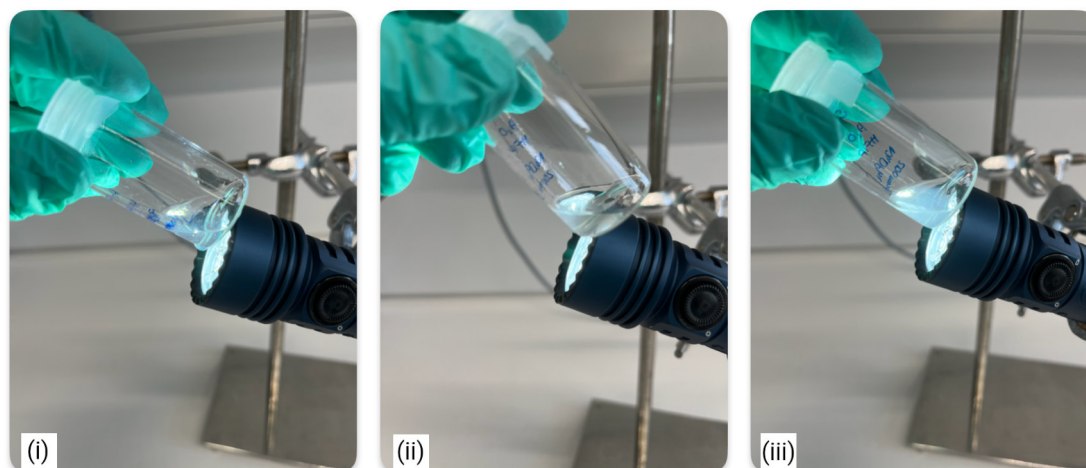


Figure 4.39.: Images of the sample containing 3.13 mmol L^{-1} of HFIP, 37.2 mmol L^{-1} of water and 200 mmol L^{-1} of NaBPh_4 . The temperature was varied from low in image (i) to high in image (iii), showing the lower phase transitions.

becomes turbid again, as depicted in Figure 4.40 (iii). At higher temperatures, however, the solution clears completely once more. In contrast to the mixture with 400 mmol L^{-1} of TPhP^+Cl^- , where both a lower and an upper critical solution temperature (LCST and UCST) were observed, the sample containing 200 mmol L^{-1} of NaBPh_4 exhibits only a lower critical solution temperature. As shown in Figure 4.39, the system becomes turbid immediately after cooling and remains so upon equilibration at room temperature. This difference highlights the distinct influence of the two antagonistic salts on the phase behavior of HFIP-water mixtures, while TPhP^+Cl^- induces two distinct phase transitions, NaBPh_4 leads exclusively to LCST-type behavior under the same experimental conditions. In comparison to the other sample, the sample with 300 mmol L^{-1} shows only partial turbidity transitions. This behavior indicates a weaker phase separation tendency at lower concentration.

For the samples containing 50 mmol L^{-1} of the antagonistic salts, no such effect was observed using this method. Nevertheless, the corresponding SAXS data follow the same theoretical trend as for the sample in which the effect was visible. Similarly, the sample containing 200 mmol L^{-1} TPhP^+Cl^- did not exhibit any observable effects with this method.

A limitation of this method is that the exact temperature of the sample inside the glass tube cannot be determined directly. In addition, the tubes had to be sealed with paraffin, since heating occasionally caused the mixtures to leak out of the glass. Another difficulty was the occurrence of partial distillation within the tubes during heating. However, this effect was also observed in the capillaries used for the SAXS measurements.

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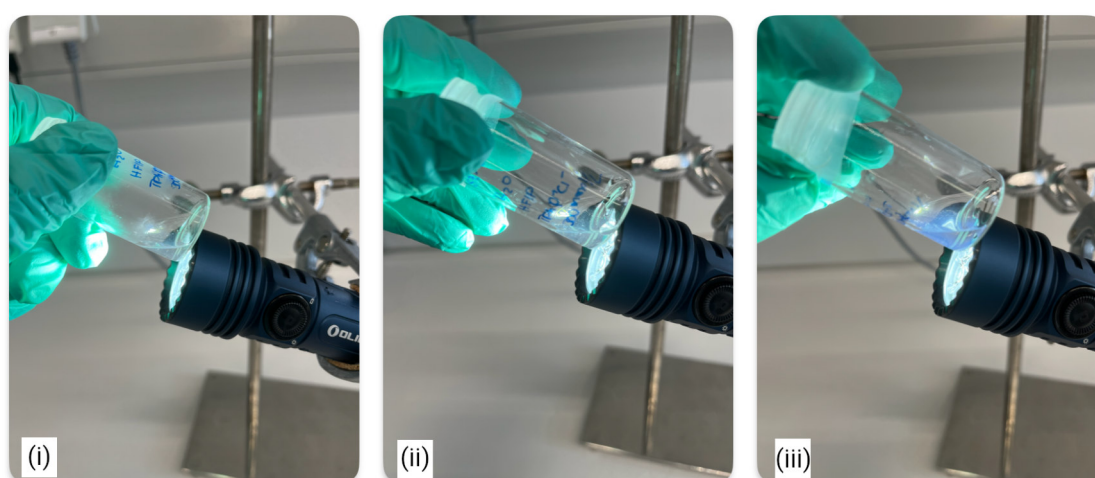


Figure 4.40.: Images of the sample containing 3.13 mmol L^{-1} of HFIP, 37.2 mmol L^{-1} of water and 300 mmol L^{-1} of TPhP^+Cl^- . The temperature was varied from low in image (i) to high in image (iii)

5. Conclusion and Outlook

5.1. Conclusion

The investigated HFIP-water mixtures exhibit clear signatures of critical-like fluctuations, which can be described within the Ornstein-Zernike framework. The scattering intensity typically increases with temperature up to a broad maximum and decreases at higher T , while transmission rises steadily, indicating enhanced homogeneity at elevated temperatures. Aging effects are consistently observed, with prolonged storage leading to reduced scattering and increased transmission, likely caused by evaporation, protonation changes, or aggregation effects. Improved sample sealing can mitigate these changes, though not entirely suppress them. In some cases, deviations from Ornstein-Zernike behavior occur, requiring alternative models such as double Lorentzian fits, which suggest additional processes like peak shifts and complex phase behavior. Overall, the results demonstrate that both HFIP concentration and sample stability critically determine the scattering response and the proximity to critical phenomena in these binary mixtures.

The comparison of HFIP-water mixtures with added pentafluoropropionic acid shows that the acid strongly modifies the scattering response. In both cases, the overall intensity is significantly reduced compared to pure HFIP-water mixtures, and the high- q decay deviates from the Ornstein-Zernike description. This suggests that more than one characteristic process contributes to the scattering, making a simple correlation length insufficient to describe the system. Although the precise intensity levels differ, the samples display a fixed peak position that does not shift with temperature, indicating the absence of a clear phase transition. Instead, the data highlight how the balance between HFIP fraction and acid concentration determines both the magnitude of scattering and the shape of the intensity profile. These findings underline the strong impact of acid addition on the structural correlations of HFIP-water systems and illustrate the limits of classical critical models in capturing their behavior.

In general the first idea of the Donor-acceptor balance within the mixtures is not sufficient to explain the observed behavior. Charges and at least one additional structural process must also be taken into account. The loss of scattering intensity cannot be attributed to HFIP or acid alone but rather arises from their interplay within the mixture. In addition, deviations from the models indicate that the current concentrations are not yet optimal to fully capture the critical transition.

The neutralization strategy using NaOH enabled the preparation of HFIP-water mixtures with different pH values and distinct scattering behavior. The results demonstrate that neutralization with NaOH plays a crucial role in controlling the structural properties of HFIP-water mixtures. By adjusting the pH, it is possible to tune the scattering response

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and shift the balance between interfacial contributions and more homogeneous correlations. In combination with the HFIP fraction, neutralization governs whether the system exhibits enhanced fluctuations or approaches a more uniform state. These findings highlight that precise control of both composition and neutralization is essential for steering the phase behavior and accessing critical phenomena such as LCST transitions.

For NaOH, an upturn in the low- q region can be observed, although the overall signal remains relatively weak. Together, these findings highlight that multiple competing processes govern the phase behavior of HFIP-water systems, and that further systematic variation of concentration and ionic conditions will be required to fully resolve the mechanisms at play.

The series of salt induced HFIP-water mixtures demonstrates that the salt concentration has a decisive influence on the scattering behavior and the resulting phase transitions. At low concentrations, only weak structural correlations are observed, while higher concentrations lead to sharper peaks, enhanced scattering, and eventually to critical fluctuations characteristic of an LCST transition. This progression highlights that increasing salt content not only amplifies correlations but also drives the system closer to phase separation. Moreover, the observed aging effects underline the sensitivity of such mixtures to time-dependent changes in composition and stability. Taken together, these results show that tuning the salt concentration provides a powerful means to control structure formation, correlation lengths, and critical behavior in HFIP-water systems, thereby opening pathways to design mixtures with tailored phase properties. Above all, the changes within the samples, after one measurement, can be seen in the HFIP-water-salt mixtures quite well.

By comparing all the datasets, in all a change in the results can be seen, after measuring them once. It is possible that they arise from destillation within the capillary or evaporation through the sealing of the capillaries. Aside from that, interactions between the different components can lead to that changes within the mixtures.

Complementary ATR spectroscopy, pH determination, and visual inspection of phase transitions provided important insights into the chemical and structural properties of the HFIP-based mixtures. ATR spectra revealed concentration-dependent changes in the O–H and C=O vibrational regions, confirming the role of hydrogen bonding, acid-base interactions, and neutralization processes in shaping the solvent environment. The pH measurements highlighted the strong influence of HFIP, pentafluoropropionic acid, and NaOH on ionization equilibria, thereby directly linking acidity control to scattering behavior. Finally, direct imaging of temperature-induced turbidity changes demonstrated the presence of both LCST- and UCST-type phase transitions in selected salt-containing mixtures, thereby confirming the SAXS results with a macroscopic probe. Together, these complementary measurements strengthen the interpretation of the scattering data and emphasize that a combined chemical, structural, and thermodynamic analysis is essential for understanding the complex phase behavior of HFIP-water systems with additives.

Taken together, these results establish a solid basis for understanding the interplay of composition, pH, and additives in HFIP-water mixtures, and they open the way for targeted future investigations.

5.2. Outlook

In future studies, several aspects should be addressed in order to improve the reliability and reproducibility of the measurements. First, the reproducibility of the samples themselves needs to be ensured, as small variations in preparation or handling can significantly influence the scattering behavior. Particular attention should be paid to the white deposits occasionally observed above the capillary closure, which may indicate the formation of peroxides or other degradation products.

From an experimental perspective, the stability of the sample holder is a critical factor. Mechanical vibrations or movement of the capillaries during the measurement can lead to distortions in the data. Therefore, the development of an improved sample holder would be beneficial.

Furthermore, the absolute sample temperature should be tracked, as the current setup provides only indirect control of the thermal environment. And the capillary must be heated up or cooled down only in a very small Bereich of the capillary.

The long-term stability of the samples also requires further investigation. Potential aging or decomposition effects could be monitored more systematically using complementary techniques such as IR, NMR, or NIR spectroscopy. In addition, problems related to partial distillation during SAXS measurements in capillaries should be carefully evaluated, as these may alter the composition of the mixtures. Possible changes in the samples over time, or under external influences such as light exposure, oxygen contact, or repeated temperature cycling, should likewise be taken into account.

Addressing these issues will not only improve data quality but also provide a deeper understanding of the intrinsic stability and reproducibility of HFIP-water based systems and their modifications.

Future work should also include the systematic investigation of lithium and potassium salts, since previous studies report that these ions exhibit a strong effect on critical parameters and may therefore further enhance or tune the phase behavior of the system.[45] Overall, the exploration of additional salts, extended temperature ranges, and complementary experimental techniques will not only deepen the fundamental understanding of HFIP-water systems, but also open pathways toward designing tailored solvent environments with tunable phase behavior.

Bibliography

- [1] S.M. Allen. Spinodal decomposition. In K.H. Jürgen Buschow, Robert W. Cahn, Merton C. Flemings, Bernhard Ilshner, Edward J. Kramer, Subhash Mahajan, and Patrick Veyssi re, editors, *Encyclopedia of Materials: Science and Technology*, pages 8761–8764. Elsevier, Oxford, 2001.
- [2] Peter W Atkins. *Chemie - einfach alles*. Wiley-VCH, Weinheim, 2., vollst.  berarb. u. erw. aufl. edition, 2006.
- [3] Peter W Atkins, Julio de Paula, Peter William Atkins, Peter Williams Atkins, P. W Atkins, P.W Atkins, Peter Atkins, P Atkins, Atkins de Paula, P Etkins, 128437782, Julio de Paula, Julio C de Paula, Julio DePaula, and 132130599. *Physikalische Chemie. [Hauptbd.]*. Wiley-VCH, Weinheim, 4., vollst.  berarb. aufl. edition, 2006.
- [4] Matthias Bartelmann, Bj rn Feuerbacher, Timm Kr ger, Dieter L st, Anton Rebhan, and Andreas Wipf. *Theoretische Physik 4 / Thermodynamik und Statistische Physik*. Springer Berlin Heidelberg : Imprint: Springer Spektrum,, Berlin, Heidelberg :, 1st ed. 2018. edition, 2018.
- [5] Markus Bier, Julian Mars, Hailong Li, and Markus Mezger. Salt-induced microheterogeneities in binary liquid mixtures. *Phys. Rev. E*, 96:022603, Aug 2017.
- [6] Bruker Optik GmbH. *TENSOR 27 User Manual*. Ettlingen, Germany, 2007.
- [7] Massimo Campanino, Dmitry Ioffe, and Yvan Velenik. Ornstein-zernike theory for finite range ising models above tc. *Probability theory and related fields*, 125(3):305–349, 2003.
- [8] F.S. Carvalho and J.P. Braga. The ornstein-zernike equation: three distinct approaches. *Revista Brasileira de Ensino de F sica*, 47:e20240407, 2025.
- [9] Benjamin Chu, Dufei Fang, and Yimin Mao. Instrumentation on multi-scaled scattering of bio-macromolecular solutions. *International Journal of Molecular Sciences (IJMS)*, 16:10016–10037, 05 2015.
- [10] Ignacio Colomer, Anna E. R. Chamberlain, Maxwell B. Haughey, and Timothy J. Donohoe. Hexafluoroisopropanol as a highly versatile solvent. *Nature reviews. Chemistry*, 1(11), 2017.
- [11] Norman B Colthup. *Introduction to infrared and Raman spectroscopy*. Acad. Press, Boston, Mass. [u.a.], 3. ed. edition, 1990.

Bibliography

- [12] Wim H de Jeu. *Basic X-Ray Scattering for Soft Matter*. Oxford University Press, Oxford, 1 edition, 2016.
- [13] P. Debye, H. R. Anderson, and H. Brumberger. Scattering by an inhomogeneous solid. ii. the correlation function and its application. *Journal of applied physics*, 28(6):679–683, 1957.
- [14] M. (Masao) Doi. *Soft matter physics*. Oxford University Press, Oxford :, first edition. edition, 2013.
- [15] J. Fahrenfort. Attenuated total reflection: A new principle for the production of useful infra-red reflection spectra of organic compounds. *Spectrochimica Acta*, 17(7):698–709, 1961.
- [16] Michael E. Fisher and B. Widom. Decay of correlations in linear systems (vol 50, 3756, 1969). *The Journal of chemical physics*, 143(20), 2015.
- [17] W. Friedrich, P. Knipping, and M. Laue. Interferenzerscheinungen bei röntgenstrahlen. *Annalen der Physik*, 346(10):971–988, 1913.
- [18] Bruker AXS GmbH. *Nanostar - enter the universe of Nanostructure Analysis*. Germnay, 2003.
- [19] Incoatec GmbH. *Montel Optics*. Germnay, 2015.
- [20] Rudolf Gross. *Festkörperphysik*. De Gruyter Studium. De Gruyter, Berlin Boston, 4., aktualisierte auflage edition, 2023.
- [21] Bob Baoping He. *Two-dimensional X-ray diffraction*. Wiley, Hoboken, N.J., 2009.
- [22] Eugene Hecht and Karen Lippert. *Optik*. De Gruyter Studium. de Gruyter, Berlin Boston, 7. auflage edition, 2018.
- [23] Christian Hoffmann. *X-ray Tube ixtube-Cu-50 Technical Data Sheet*. Gesestacht, Germany, 2016.
- [24] Bruker AXS Inc. *M88-Exx10 VÅntec-2000 User Manual*. Madison, USA, 2007.
- [25] Max-Planck Institut. Unravelling the workings of ‘miracle solvent’ hexafluoroisopropanol — mpip-mainz.mpg.de. https://www.mpip-mainz.mpg.de/986850/20241030_Hunger, 2024. [Accessed 24-09-2025].
- [26] John David Jackson. *Klassische Elektrodynamik*. De Gruyter,, Berlin ; Boston :, reprint 2020 edition, 2020.
- [27] John G Kirkwood. Statistical mechanics of liquid solutions. *Chemical reviews*, 19(3):275–307, 1936.
- [28] Dr. L.S.Ornstein and F.Zernike. Accidental deviations of density and opalescence at the critical point of a single substance. *KNAW*, pages 793–806, 09 1914.

- [29] National Center for Biotechnology Information. Pubchem compound summary for cid 13529, 1,1,1,3,3,3-hexafluoro-2-propanol. https://pubchem.ncbi.nlm.nih.gov/compound/1_1_1_3_3_3-Hexafluoro-2-propanol, 2025. Retrieved August 13, 2025.
- [30] National Center for Biotechnology Information. Pubchem compound summary for cid 14798, sodium hydroxide. <https://pubchem.ncbi.nlm.nih.gov/compound/Sodium-Hydroxide>, 2025. Retrieved August 13, 2025.
- [31] National Center for Biotechnology Information. Pubchem compound summary for cid 62356, pentafluoropropionic acid. <https://pubchem.ncbi.nlm.nih.gov/compound/Pentafluoropropionic-acid>, 2025. Retrieved August 13, 2025.
- [32] National Center for Biotechnology Information. Pubchem compound summary for cid 67542, perfluorohexanoic acid. <https://pubchem.ncbi.nlm.nih.gov/compound/Perfluorohexanoic-Acid>, 2025. Retrieved August 13, 2025.
- [33] National Center for Biotechnology Information. Pubchem compound summary for cid 9882740, triphenylphosphine hydrochloride. <https://pubchem.ncbi.nlm.nih.gov/e>, 2025. Retrieved August 13, 2025.
- [34] National Institute of Standards and Technology (NIST). Nist chemistry webbook, 2025. Retrieved September 12, 2025.
- [35] Akira Onuki. *Phase transition dynamics*. Cambridge Univ. Press, Cambridge [u.a.], 1. publ. edition, 2002.
- [36] G Pagnini and R. K Saxena. A note on the voigt profile function. *arxiv*, 2008.
- [37] Wolfgang Pfeiler. *Alloy physics : a comprehensive reference*. Wiley-VCH, Weinheim, 2007.
- [38] Michael Plischke. *Equilibrium statistical physics*. World Scientific, Singapore [u.a.], 2007.
- [39] Günther Porod. Theorie der diffusen röntgenkleinwinkelstreuung an kolloiden systemen. *Zeitschrift für Naturforschung. A, A journal of physical sciences*, 4(6):401–414, 1949.
- [40] W. C. Röntgen. Ueber eine neue art von strahlen. *Annalen der Physik*, 300(1):12–17, 1898.
- [41] John M. Seddon. Structure of the inverted hexagonal (hii) phase, and non-lamellar phase transitions of lipids. *Biochimica et Biophysica Acta (BBA) - Reviews on Biomembranes*, 1031(1):1–69, 1990.
- [42] Shri Singh. *Liquid crystals : fundamentals*. World Scientific, Singapore ; New Jersey :, 2002.

Bibliography

- [43] Lawrie B. Skinner, Chris J. Benmore, and John B. Parise. Area detector corrections for high quality synchrotron x-ray structure factor measurements. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 662(1):61–70, 2012.
- [44] Norbert Stribeck. *X-ray scattering of soft matter : with 6 tables*. Springer laboratory manuals in polymer science. Springer, Berlin [u.a.], 2007.
- [45] Toshiyuki Takamuku, Yuki Kouda, and Takuya Shimomura. Heat-induced phase separation of alkali chloride–hfp–water mixtures. *Journal of Molecular Liquids*, 189:113–121, 01 2014.
- [46] Takahiro To, Yohei Hatomoto, Tatsuya Umecky, and Toshiyuki Takamuku. Solvation power of hfp for the hydrophilic and the hydrophobic moieties of l-leucine studied by md, ir, and nmr techniques. *Journal of Molecular Liquids*, 230:261–270, 2017.
- [47] Koji Yoshida, Toshio Yamaguchi, Tomohiro Adachi, Toshiya Otomo, Daisuke Matsuo, Toshiyuki Takamuku, and Nobuyuki Nishi. Structure and dynamics of hexafluoroisopropanol–water mixtures by x-ray diffraction, small-angle neutron scattering, nmr spectroscopy, and mass spectrometry. *Chemical Physics - CHEM PHYS*, 119, 09 2003.

A. Appendix

A.1. Used Programs

Python:

- `scipy.optimize`
- `numpy`
- `fabio`
- `io`
- `matplotlib`
- `pandas`

other Programs:

- Avogadro - simulate the molecules and skeletal formula
- Chemdraw
- TeXstudio
- TikZ
- Blender with textures and shaders
- Gimp
- Freeform
- Dataqueeze

A.2. Tables

A. Appendix

Name	CAS-Number	chemical formula	molar mass (g mol ⁻¹)	density (g cm ⁻³)	Acidity (pK _a)	Basicity (pK _b)	Dipole moment (Cm)
Hexafluoroisopropanol (HFIP)	920 – 66 – 1	C ₃ H ₂ F ₆ O	168.04	1.596	9.3	4.7	2.05
Pentafluoropropionic acid	422 – 64 – 0	C ₃ HF ₅ O ₂	164.03	1.561	0.38	13.62	
Perfluorohexanoic acid	307 – 24 – 4	C ₆ HF ₁₁ O ₂	314.0	1.762	0.5	13.5	
Sodium Hydroxid	1310 – 73 – 2	NaOH	39.997	2.13	13.9	0.1	6.9
Tetraphenylphosphonium chloride	2001 – 45 – 8	C ₂₄ H ₂₀ PCl	374.84	1.27	-	-	-
Sodium Tetraphenylborate	143 – 66 – 8	C ₂₄ H ₂₀ BNa	342.22	1.216	-	-	-
Water	7732 – 18 – 5	H ₂ O	18.02	0.997	14	0	1.855

Dielectric constant	Boiling Temperature (K)	Melting Temperature (K)	Absorption length X-ray (μm)	Solubility in H ₂ O (molL ⁻¹)	Hydrogen Bond Acceptor	Hydrogen Donator
16.7	58 °C	-3 °C	488	5.95	7	1
8.20	160 °C	-	515	0.5	7	1
-	157 °C	-	422	15.7	13	1
57.5	1390 °C	681 °C	0.04032	31.5	1	1
-	246 °C	272 °C	469	1	1	0
-	275 °C	300 °C	1684	0.5	1	0
78.3	100 °C	0 °C	971	-	2	2

Table A.2.: Properties of the used chemicals [30], [29], [31], [33],[10] and [32]

A.3. Macro for Temperature controlled measurements

```

1  ! What does this macro do:
2  ! Start Generator
3  ! Control Temperature
4  ! Single Run Scan
5
6
7  ! How to use this macro:
8  ! Input variables: integration time I, x and y Position, start and stop
   Temperature, Delta T
9  ! Attention: The variables are only allowed to have one letter as description
10 ! Attention: For using the while loop , the RUN must be increased for every
   Single Run sequence
11 ! start the macro via SAXS Command Mode: @nameofthmacro.slm
12
13
14 ! Generator
15 GONIOMETER /GENERATOR 50.0  1.00 /WAIT
16
17 ! Set integration time
18 #LET %I=500
19
20 ! Sample, Title, Name
21 ! Set Goniometer position x, y
22 #Let %M=SZ9
23 #Let %L=HFIPH20
24 #LET %A=46.5
25 #LET %B=112
26
27 #Let %P=SZ8
28 #Let %O=HFIPH20
29 #LET %G=55.5
30 #LET %H=112
31
32 #Let %T=SZ7
33 #Let %R=HFIPH20
34 #LET %J=64.5
35 #LET %K=112
36
37 ! Start temperature at
38 #LET %S=20
39 ! Stop temperature at
40 #LET %E=90
41
42 ! Increase temperature by
43 #LET %D=10
44 ! FileCounter
45 #LET %C=001

```

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```

46 #WHILE (%S<=%E) DO
47 GONIOMETER /TEMP %S /RAMP=10 /HOLD=2 /WAIT
48
49
50 wait 30
51
52 SCAN /SINGLERUN 1 /START=35 /WIDTH=0.0 /SCANTIME=150 /FIXED=40 &
53 /AXIS=X /RSW=22.000 /TITLE='N' /SAMPLE=empty /NUMSAMPLE=0 /NAME=HFIP &
54 /RUN=0 /FRAMENO=%C /DISPLAY=7 /REALTIME /CLEAR
55
56 SCAN /SINGLERUN 1 /START='%J' /WIDTH=0.0 /SCANTIME='%I' /FIXED='%K' &
57 /AXIS=X /RSW=22.000 /TITLE='%U' /SAMPLE='%T' /NUMSAMPLE=0 /NAME=HFIP &
58 /RUN=1 /FRAMENO=%C /DISPLAY=7 /REALTIME /CLEAR
59
60 SCAN /SINGLERUN 1 /START='%G' /WIDTH=0.0 /SCANTIME='%I' /FIXED='%H' &
61 /AXIS=X /RSW=22.000 /TITLE='%U' /SAMPLE='%P' /NUMSAMPLE=0 /NAME=HFIP &
62 /RUN=1 /FRAMENO=%C /DISPLAY=7 /REALTIME /CLEAR
63
64 SCAN /SINGLERUN 1 /START='%A' /WIDTH=0.0 /SCANTIME='%I' /FIXED='%B' &
65 /AXIS=X /RSW=22.000 /TITLE='%U' /SAMPLE='%M' /NUMSAMPLE=0 /NAME=HFIP &
66 /RUN=3 /FRAMENO=%C /DISPLAY=7 /REALTIME /CLEAR
67
68 ADD 1 /CLEAR /COUNTS=10000000 /DISPLAY=7 /REALTIME /RESET=0 /SHUTTER &
69 /SLAM=$null /BARTIME=0.0 /SLAM=$null
70
71 #LET %S=%S+%D
72 #INC %C
73 #WEND
74
75 menu

```

Listing A.1: Macro for Temperature controlled SAXS measurements

Configuration	Angular range (°)	Q-Range (nm ⁻¹)
Long	0.1 – 4	0.08 – 2.2
Short	1 – 27	0.8 – 19

Table A.3.: Brucker AXS Nanostar Properties

A.4. Images



Figure A.1.: HFIP sample with white deposits have formed at the top of the capillary near the closure