

Review

Phase Behaviour of Binary Mixtures Involving Near-Critical and Supercritical Carbon Dioxide—A Review

Pradnya N. P. Ghoderao and Patrice Paricaud * 

UCP, ENSTA Paris, Institute Polytechnique de Paris, 828 Boulevard des Maréchaux, 91762 Palaiseau, France

* Correspondence: patrice.paricaud@ensta.fr

Abstract

Near-critical and supercritical carbon dioxide (SC-CO₂) is extensively utilized in high-pressure separation, extraction, polymer processing, and carbon capture and utilization (CCU) technologies owing to its tunable density, low viscosity, high diffusivity, and environmentally benign nature. Reliable phase equilibrium data are indispensable for process design and optimization, especially in the near-critical region characterized by pronounced non-idealities, high compressibility, and density fluctuations. This review synthesizes experimental phase behaviour studies for binary mixtures of CO₂ with diverse components, including hydrocarbons, alcohols, ethers, esters, ketones, water, monomers/polymers, ionic liquids (ILs), and deep eutectic solvents (DESs), compiling extensive vapour–liquid equilibrium (VLE), liquid–liquid equilibrium (LLE), and critical data across industrially relevant pressure (up to 40 MPa) and temperature (up to 400 K) ranges. It critically evaluates analytical (sampling and non-sampling) and synthetic methodologies, addressing challenges in CO₂-rich phase handling, depressurization artefacts, and near-critical phenomena, while assessing data consistency against established reliability criteria. Key trends emerge, such as enhanced solubility with increasing pressure and CO₂ density, chain-length dependencies in hydrocarbons and alcohols, and Lewis acid–base interactions driving solvation in polar systems. The review highlights gaps in multicomponent data and proposes integrating high-quality experiments with advanced thermodynamic modelling to enhance predictive accuracy. Future directions emphasize high-precision in situ techniques, expanded datasets for complex mixtures, and novel CO₂-philic solvents to advance sustainable SC-CO₂ applications.

Keywords: supercritical carbon dioxide; high-pressure phase equilibria; binary mixtures; phase equilibrium measurements; ionic liquids and deep eutectic solvents; carbon capture and utilization (CCU)



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1. Introduction

1.1. CO₂: From an Environmental Challenge to a Valuable Resource

Human activities are driving a rise in atmospheric CO₂ levels, which is a major contributor to climate change. This is caused by emissions from various sectors like energy production, transportation, the manufacturing industry, fuel use, electricity generation, and agriculture. China, India, Canada, the USA, Japan, and Russia are the world's leading consumers of energy and emitters of greenhouse gases [1,2]. This has a cascade effect leading to several problems such as global warming, sea level rise, ocean acidification, disrupted ecosystems, etc. [3]. Even with aggressive transitions to renewable energy sources, reducing atmospheric CO₂ to safe levels remains a significant challenge. Carbon

capture and utilization (CCU) aim to reduce emissions by capturing CO₂ and subsequently converting it into value-added products, with many of the associated challenges arising during the utilization and downstream processing stages rather than the initial capture step. CO₂ possesses certain intrinsic limitations from a chemical and thermodynamic standpoint, particularly during utilization and downstream processing stages. While some of these limitations are specific to CO₂, others are common characteristics shared by many solvents [4]: (1) the relatively high vapour pressure and critical point of CO₂ necessitate expensive equipment for both industrial processes and laboratory settings. Furthermore, exothermic reactions present a particular challenge in CO₂ due to the inherently high-pressure environment. (2) CO₂'s inherent limitations as a solvent, stemming from its low polarizability per unit volume and low cohesive energy density, manifest as a key challenge for its widespread adoption. This weakness is reflected in its low dielectric constant ($\epsilon \approx 1.5$) across both liquid and supercritical states. These properties combine to hinder CO₂ effectiveness in two ways: firstly, by limiting certain chemical reactions that require polar environments, and secondly, by reducing its solvating power. Consequently, dissolving many compounds of interest requires uneconomically high pressures compared to more polar solvents. This highlights CO₂'s greatest flaw, its inability to readily solvate a broad range of compounds, which significantly hinders its commercial viability. (3) CO₂'s Lewis acidity can lead to unwanted side reactions with nucleophilic (electron-donating) species commonly used in organic chemistry. This can include reactions with substrates, catalysts, or even starting materials like amines. These side reactions can slow down the desired reaction, alter solubility of components, or deactivate catalysts, ultimately hindering overall reaction efficiency.

The effectiveness of carbon capture and utilization (CCU) technologies depends on a robust understanding of the thermodynamic phase behaviour of CO₂-containing mixtures. Such understanding underpins the design and optimization of separation and utilization processes across different stages of CCU, particularly during capture-relevant separations and downstream conversion and processing. Phase behaviour studies contribute to CCU technologies in several ways. (1) For capture-relevant separations, knowledge of the pressure- and temperature-dependent solubility of CO₂ in physical and chemical solvents enables the identification of appropriate operating conditions for efficient CO₂ separation from accompanying gas components. (2) Thermodynamic phase behaviour studies play a critical role in the development and optimization of CO₂ conversion processes. Supercritical CO₂, for instance, serves as a powerful solvent in various extraction applications (e.g., in decaffeination or essential oil extraction). Elucidating the interaction between CO₂ and target molecules within a mixture is essential for determining optimal operating conditions that maximize extraction efficiency. Similarly, in CO₂ conversion processes targeting fuel or chemical production, phase behaviour studies provide valuable insights for predicting reaction yields and product purities. (3) Guaranteeing the safety and efficiency of CO₂ transportation and storage necessitates a comprehensive understanding of its phase behaviour. CO₂ can be transported in diverse forms, encompassing compressed gas, supercritical fluid, solid, and even dissolved states within liquids. Phase behaviour studies provide the ability to predict the behaviour of CO₂ under different pressure and temperature conditions encountered during transport. This knowledge is instrumental in ensuring safe and secure CO₂ handling. Furthermore, for geological storage of CO₂, such as in depleted oil reservoirs, understanding the phase behaviour allows for the prediction of stored CO₂ stability, thereby mitigating potential leakage risks. Recent studies have explored integrated approaches combining hydrogen-blended natural gas storage with carbon sequestration in fractured carbonate reservoirs, providing insights into gas mixing and storage efficiency, including the effects of non-Darcy flow, reservoir deformation,

multicomponent transport, and numerical optimization methods for improved operational performance [5].

Liquid and supercritical CO₂ present attractive alternatives to conventional organic solvents in solvent selection. While organic solvents have historically dominated due to their favourable polarity for many solutes, CO₂ offers a more environmentally benign option. Its abundance, non-toxic character, and lack of contribution to smog formation, along with its ability to replace certain regulated organic solvents historically associated with environmental concerns, make CO₂ a responsible choice for a wide range of applications. However, limitations associated with CO₂ utilization also exist, as discussed earlier. Furthermore, process optimization for CO₂-based applications can be more complex due to the requirement for precise control over multiple parameters, including pressure, temperature, and flow rates. Ongoing research and development efforts focused on optimizing CO₂-based processes hold the potential to significantly improve their efficiency and versatility. This continued advancement has paved the way for CO₂ to replace traditional organic solvents in a wider array of applications.

Several review articles have addressed high-pressure phase equilibrium data and experimental methodologies for fluid systems, including CO₂-containing mixtures [6–8]. In addition, a limited number of reviews have focused on specific aspects of fundamental CO₂ phase behaviour, such as solubility of solids and polymers in subcritical and supercritical CO₂, thermodynamic concepts, and measurement techniques [9–13]. In contrast, the majority of fundamental investigations of CO₂ phase behaviour with solvents, polymers, and solutes are reported as individual experimental studies rather than consolidated, application-spanning reviews (Tables in Supplementary Materials). Accordingly, the present review aims to integrate fundamental CO₂ phase behaviour studies with experimental methodologies, while highlighting key challenges, data gaps, and future research directions.

1.2. Supercritical Solvents: CO₂ Leading the Charge

Despite the extended utilization of supercritical fluids (SCFs) across diverse industrial applications over a span of six decades, a comprehensive understanding of their distinctive thermophysical characteristics only emerged during the early 1970s. Universal scaling laws between thermodynamic variables are observed in the near-critical region [14,15]. SCFs possess advantageous characteristics that render them suitable for demanding extraction processes. Key properties of an SCF include density, viscosity, diffusivity, heat capacity, and thermal conductivity. The elevated densities of SCFs facilitate increased solubilization of compounds, while their low viscosities coupled with heightened diffusivity enable penetration into solid materials and promote flow with reduced friction. Adjusting the temperature and pressure beyond the critical points alters the properties of SCFs, augmenting their capacity to infiltrate source materials and extract specific molecules more effectively [16]. Small alterations in pressure and temperature can readily modify the density of a pure supercritical fluid. The Joule–Thomson effect often causes a substantial decrease in temperature when pressure is reduced. This phenomenon influences phase behaviour significantly and serves as a fundamental principle for various practical applications [17]. Surface tension is not observed in SCFs. A list of commonly used SCFs is presented in Table S1 in the Supplementary Materials [18,19].

The increasing global demand for high-quality, safe foods and medicines, alongside environmental concerns and a preference for natural substances, has driven strict regulations on toxin levels. In response, there has been a thrust towards eco-friendly extraction technologies/green extraction for ‘natural’ products, highlighting the need for non-toxic solvents [20,21]. Supercritical fluid extraction has emerged as a superior alternative to

traditional methods in food, pharmaceutical, and chemical industries, offering cleaner processes and higher yields of extracts with extended shelf life and enhanced blending characteristics [22,23]. This shift aligns with ‘industrial ecology’ principles, promoting coexistence between ecosystems and industries while emphasizing the cost-effectiveness of pollution prevention via green chemistry and engineering. The study by Costa et al. [24] reveals that SC-CO₂ can effectively modulate reaction selectivity, demonstrating its potential to enhance the production of specific products in catalytic processes by adjusting reaction conditions. Experimental studies have shown that density differences between supercritical CO₂ and CH₄ significantly influence their adsorption capacities in coal and anthracite reservoirs, highlighting the importance of fluid properties in designing efficient storage systems. Various industrial applications and chemical reactions involving SCFs are illustrated in Figure 1.

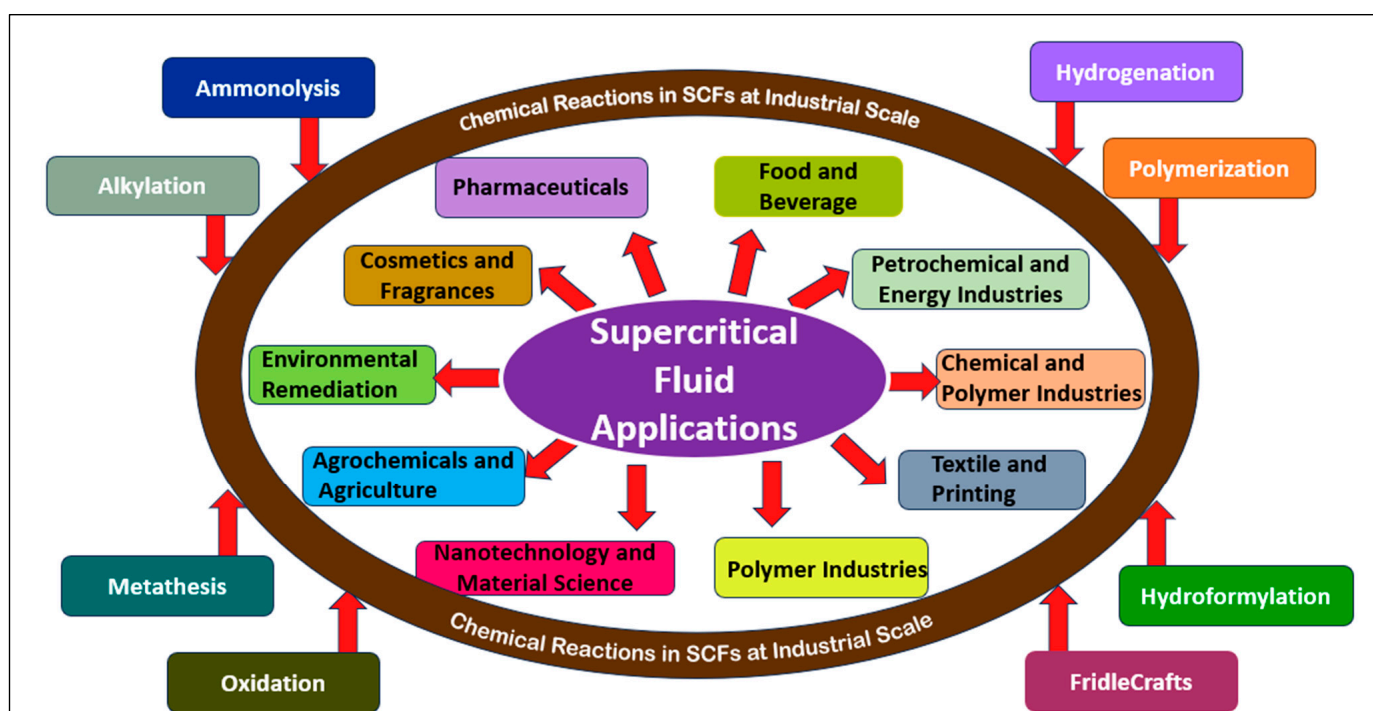


Figure 1. Chemical reactions and industrial applications of supercritical fluids.

A search for the keyword “supercritical carbon dioxide” reveals that Elsevier has published 41,076 articles on this topic since 2000. A more detailed breakdown of the yearly publications within Elsevier is provided in Figure 2. The trend clearly demonstrates a consistent increase in the number of articles published on supercritical CO₂ each year, indicating a growing interest among researchers in this field. Notably, the Journal of Supercritical Fluids stands out as the publisher of the highest number of articles, totaling 4069 publications to date.

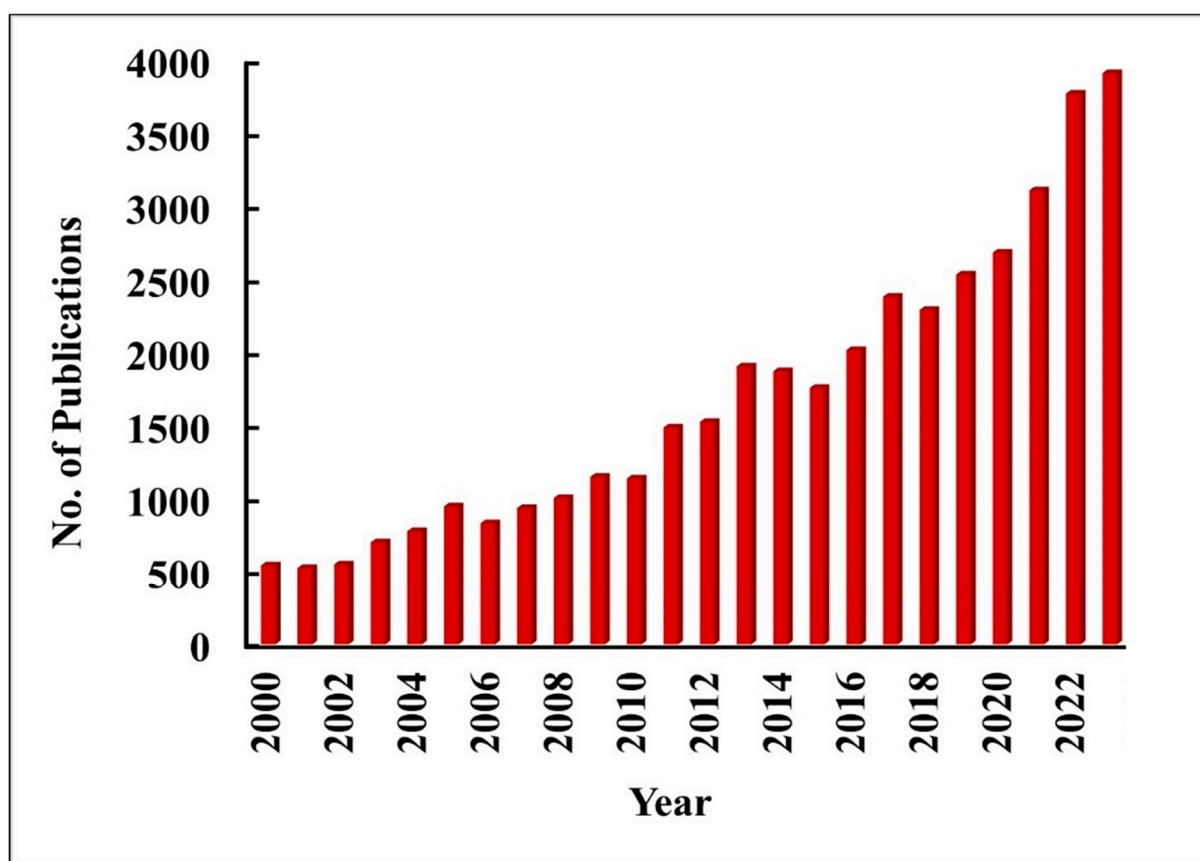


Figure 2. The number of publications in Elsevier with the keyword “supercritical carbon dioxide” since 2000.

Across all conceivable fluids (Table S1), SC-CO₂ has emerged as the most widely used solvent in both research and industrial applications for several compelling reasons [25,26]: (1) moderate critical point; (2) non-corrosive, non-flammable, and with limited toxicity; (3) cheap and recyclable; (4) exhibits high miscibility with a wide range of organic solvents; (5) adaptable and versatile extraction processes capable of handling multiple products using a singular solvent, with or without an additional co-solvent; (6) easy adjustment of solvency and selectivity by altering temperature and pressure settings; and (7) a wide spectrum of solvent properties including density, polarity, and viscosity within a singular solvent, a feature not commonly found in traditional liquid solvents. The properties of CO₂ are summarized in Figure 3 [27,28]. Due to these illustrated properties, researchers are predominantly interested in SC-CO₂, which is used in more than 90% of supercritical fluid extraction processes [29] and 80% of overall research in the supercritical fluid based technology and processes [30]. The unique characteristics of SC-CO₂ render it highly suitable for substituting organic solvents in polymer processing [31,32]. Extensive studies have examined the miscibility, phase separation, and alterations in morphology of polymer solutions in high-pressure supercritical fluids [33]. SC-CO₂ serves as an efficient diluent for polymer melts, markedly augmenting free volume, consequently enhancing material processability by reducing viscosity and interfacial tension [17].

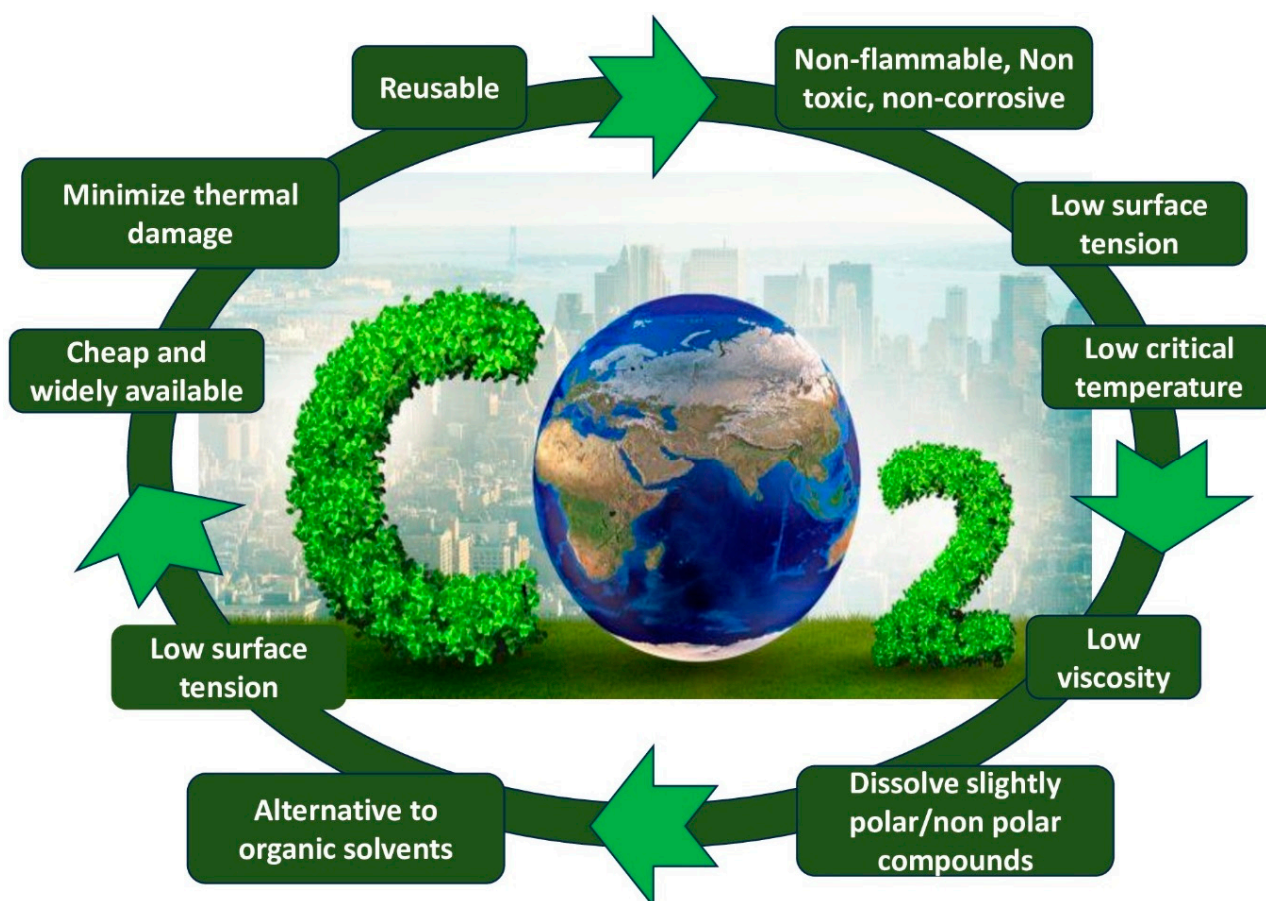


Figure 3. The properties of CO₂.

One recognized limitation of SC-CO₂ is its inherent nonpolar nature. Research indicates that hydrocarbons and other organic compounds featuring lower polarity and molecular weights (MWs) below 250 Da demonstrate exceptional solubility in SC-CO₂. This process can be conducted at relatively lower pressures, typically ranging between 7.5 and 10 MPa. Moderately polar components within the MW range of 250 Da to 400 Da exhibit moderate solubility in SC-CO₂, necessitating higher pressures for effective extraction. Conversely, highly polar substances with molecular weights exceeding 400 Da are nearly insoluble in SC-CO₂ [34]. Nonetheless, this perceived drawback can be effectively addressed by incorporating a polar co-solvent, to change non-polar nature of SC-CO₂ [35,36]. This addition forms a homogeneous binary mixture with SC-CO₂, preserving the essential traits of a supercritical fluid solvent. By employing this method, SC-CO₂ can enhance its polarity, thereby boosting its solvent capability for highly polar or large molecular weight compounds [37]. The incorporation of co-solvents or modifiers typically occurs through two primary methods: firstly, by blending the modifier with the flow of CO₂, and secondly, by combining the modifier directly with the raw material within the extraction vessel [38]. However, incorporating substantial amounts of co-solvents can alter the critical properties of the fluid, potentially diminishing its selectivity in the extraction process. Ethanol, ethyl acetate, and conceivably water stand out as natural food-grade co-solvents [26].

1.3. Objectives and Scope of the Review Article

Objectives: The phase behaviour of CO₂-containing systems plays a central role in governing solubility, phase stability, and separation behaviour under both subcritical and supercritical conditions. Despite extensive experimental studies, the available knowledge is fragmented across individual investigations and experimental approaches, making it

challenging to obtain a unified understanding of CO₂ phase equilibria. This review article aims to offer a comprehensive and critical analysis of the phase behaviour exhibited by binary mixtures involving near-critical and supercritical carbon dioxide. In particular, the focus is placed on consolidating dispersed experimental findings and methodological approaches related to CO₂ phase equilibria. In this review, a comprehensive compilation of experimental phase equilibrium data for various binary systems involving near-critical and supercritical CO₂ is presented. Extensive data tables are provided in the Supplementary Materials that systematically document phase behaviour for diverse binary mixtures, including hydrocarbons, alcohols, ethers, and other solute systems.

These detailed datasets are integral to understanding the nuances of phase equilibria, offering valuable insights for researchers working on CO₂-containing systems under high-pressure conditions. By systematically analyzing these binary systems, this review addresses fragmentation in the existing literature and provides a robust foundation for future studies in this domain. The primary objectives of the review are as follows: (1) *Elucidation of Governing Principles*: To elucidate the fundamental principles underlying phase behaviour in SC-CO₂ systems. This encompasses a detailed exploration of the roles of pressure, temperature, component properties, and intermolecular interactions in dictating phase equilibria and critical phenomena. (2) *Systematic Examination of Experimental Methodologies*: To critically evaluate and compare various experimental techniques employed to investigate high-pressure phase equilibria in SC-CO₂ systems. This includes assessing the accuracy, reliability, and limitations of different high-pressure experimental setups and measurement techniques. (3) *Implications for CO₂-Based Systems*: To discuss how an improved understanding of CO₂ phase behaviour supports the interpretation of experimental data and informs the development of CO₂-based separation and utilization studies. (4) *Identification of Knowledge Gaps and Future Research Directions*: To critically assess existing experimental data and methodologies in order to identify key knowledge gaps, inconsistencies, and limitations, and to use these insights to formulate informed future research directions.

Scope: The scope of this review encompasses a thorough investigation of binary systems where CO₂ is one of the components. The review focuses on the following aspects: (1) *Range of Components*: The second component in the binary mixtures can include a wide array of substances such as organic solvents, polymers, ionic liquids, hydrocarbons, alcohols, ethers, ketones, esters, water, monomers, and deep eutectic solvents. The review examines the phase behaviour of CO₂ with these diverse components across a broad spectrum of conditions. (2) *Pressure and Temperature Ranges*: Emphasis is placed on the pressure and temperature ranges characteristic of near-critical and supercritical conditions. This includes a detailed examination of the phase behaviour in these specific regimes and its impact on system properties. (3) *Fundamental and Methodological Aspects*: The review primarily addresses fundamental aspects of phase behaviour, including phase equilibria, critical phenomena, and solubility, together with experimental methodologies used to generate and interpret high-pressure phase equilibrium data. (5) *Emerging Trends and Future Prospects*: The review also casts a forward-looking perspective on emerging trends and potential advancements in the study of CO₂ mixture phase behaviour. This includes exploring innovative research avenues and potential applications that could drive future developments in CO₂ utilization. By delineating these objectives and scope, this review article provides a structured and comprehensive framework for exploring the complex phase behaviour of CO₂ mixtures.

2. Supercritical Fluids with Emphasis on CO₂

2.1. Supercritical Fluids CO₂: Definition and Key Properties

The initial observation of a SCF occurred in 1822, credited to Baron Charles Cagniard de la Tour. He observed a shift in solvent characteristics at specific pressure and temperature conditions. Subsequently, in 1869, Thomas Andrews coined the term “critical point” while studying the impact of temperature and pressure on partially liquefied carbonic acid within sealed glass tubes. He precisely defined this critical point as the unique temperature (T_c) and pressure (P_c) situated on the phase equilibrium curve, representing the conditions where two distinct phases cease to exist simultaneously [39]. A supercritical fluid denotes a substance existing at conditions surpassing its critical point concerning temperature and pressure. The critical point denotes the utmost temperature and pressure under which a substance can maintain equilibrium in both vapour and liquid states. At this juncture, the fluid embodies characteristics of both its gaseous and liquid phases. It permeates solids akin to gases while exhibiting dissolution capabilities comparable to liquids [40]. In brief, achieving the supercritical region involves two approaches: (i) elevating the pressure above the substance’s critical pressure while maintaining a constant temperature, then surpassing the critical temperature at a stable pressure; or (ii) initially increasing the temperature beyond the critical temperature and subsequently raising the pressure above the critical pressure [20]. While many substances can be brought into a supercritical state, CO₂ is by far the most extensively studied and industrially relevant supercritical fluid. This predominance arises from its moderate critical constants ($T_c = 304.13$ K, $P_c = 7.38$ MPa), non-flammability, low toxicity, chemical inertness under many conditions, low cost, and ease of recycling.

SC-CO₂ exhibits a unique combination of gas-like and liquid-like properties that are highly sensitive to pressure and temperature in the near-critical region. Small variations in pressure near the critical point induce large changes in density, enabling fine tuning of solvent strength without changing chemical composition. This density tunability is a defining advantage of SC-CO₂ and underpins its widespread use in extraction, separation, reaction, and materials processing. Compared with conventional organic solvents, SC-CO₂ possesses low viscosity and high diffusivity, which enhance mass transfer and facilitate penetration into porous solids. At the same time, its liquid-like densities at elevated pressures allow significant solvation of low-to moderately polar compounds. The absence of surface tension in the supercritical state further improves wetting and transport phenomena, particularly in solid–fluid systems. The comparison of physical and chemical properties of CO₂ in gas, liquid, and supercritical phases is given in Figure 4.

2.2. Phase Behaviour of Pure CO₂ near and Above the Critical Point

The phase behaviour of pure carbon dioxide forms the thermodynamic foundation for understanding phase equilibria in CO₂-containing binary systems. As illustrated in the pressure–temperature (P – T) projection of the state surface (Figure 5a), CO₂ exhibits conventional solid, liquid, and vapour regions at subcritical conditions, separated by well-defined coexistence curves. The vapour–liquid equilibrium (VLE) curve terminates at the critical point ($T_c = 304.13$ K, $P_c = 7.38$ MPa), beyond which the distinction between liquid and vapour phases vanishes. Above the critical point, CO₂ exists as a single supercritical phase characterized by continuous and smooth changes in thermophysical properties with pressure and temperature. This behaviour is more clearly understood by examining the full thermodynamic state surface represented in pressure–temperature–specific volume space (Figure 5b) and its projection onto the pressure–specific volume ($P - 1/\rho$) plane (Figure 5c). In these representations, the liquid–vapour coexistence region appears as a finite dome,

with the apex corresponding to the critical point. Beyond this apex, isotherms no longer intersect phase boundaries, indicating the absence of first-order phase transitions.

Gas ($P = 1$ atm, $T = 25$ – 30 °C)

Density	Diffusivity	Viscosity
1.8–2 g/L	10–16 mm ² /s	(1.4–1.6)10 ^{−5} Pa.s

Liquid ($P = 60$ – 70 bar, $T = 20$ – 25 °C)

Density	Diffusivity	Viscosity
900–1100 g/L	0.05–0.2 mm ² /s	(7–1)10 ^{−5} Pa.s

Supercritical fluid ($P = P_c$, $T = T_c$)

Density	Diffusivity	Viscosity
200–900 g/L	0.1–1 mm ² /s	(3–8) 10 ^{−5} Pa.s

Figure 4. Properties of vapour, liquid, and supercritical CO₂.

In the near-critical region of CO₂, small variations in pressure or temperature led to disproportionately large changes in density, compressibility, and heat capacity. These critical anomalies strongly influence solubility, mass transfer, and phase equilibria in CO₂-based mixtures. In particular, the steep density gradients observed near the critical point (Figure 5c) are responsible for the exceptional tunability of SC-CO₂ as a solvent. This sensitivity underpins many applications of SC-CO₂ but simultaneously demands highly accurate phase equilibrium data. For practical applications, the behaviour of CO₂ is often described using reduced variables ($Tr = T/T_c$ and $Pr = P/P_c$). The near-critical and supercritical regions most relevant to phase equilibrium studies typically span $Tr \approx 0.95$ – 1.2 and $Pr \approx 1.0$ – 3.0 . Within this domain, CO₂ transitions smoothly from gas-like to liquid-like densities without crossing a phase boundary, a feature that is central to its role as a tunable solvent in extraction, separation, and reaction processes.

2.3. Solvent Characteristics and Limitations of SC-CO₂

Despite its many advantages, SC-CO₂ is intrinsically nonpolar, with a low dielectric constant and limited cohesive energy density. As a result, its solvent power is highest for nonpolar or weakly polar compounds with relatively low molecular weight. Highly polar, strongly associating, or high-molecular-weight compounds generally exhibit low solubility in SC-CO₂ under practical conditions. The quadrupolar nature of CO₂ enables specific interactions, including dipole–quadrupole and Lewis acid–base interactions, which play a critical role in solubilizing compounds containing carbonyl, ether, or other electron-donating functional groups. These interactions are highly sensitive to CO₂ density and temperature, reinforcing the need for reliable phase equilibrium measurements.

To overcome solubility limitations, small amounts of polar co-solvents (modifiers) such as alcohols or esters are often added. While effective, the addition of co-solvents alters the critical properties and phase behaviour of the system, complicating both experimental measurement and thermodynamic modelling. Understanding these effects requires systematic phase equilibrium data for CO₂-containing mixtures.

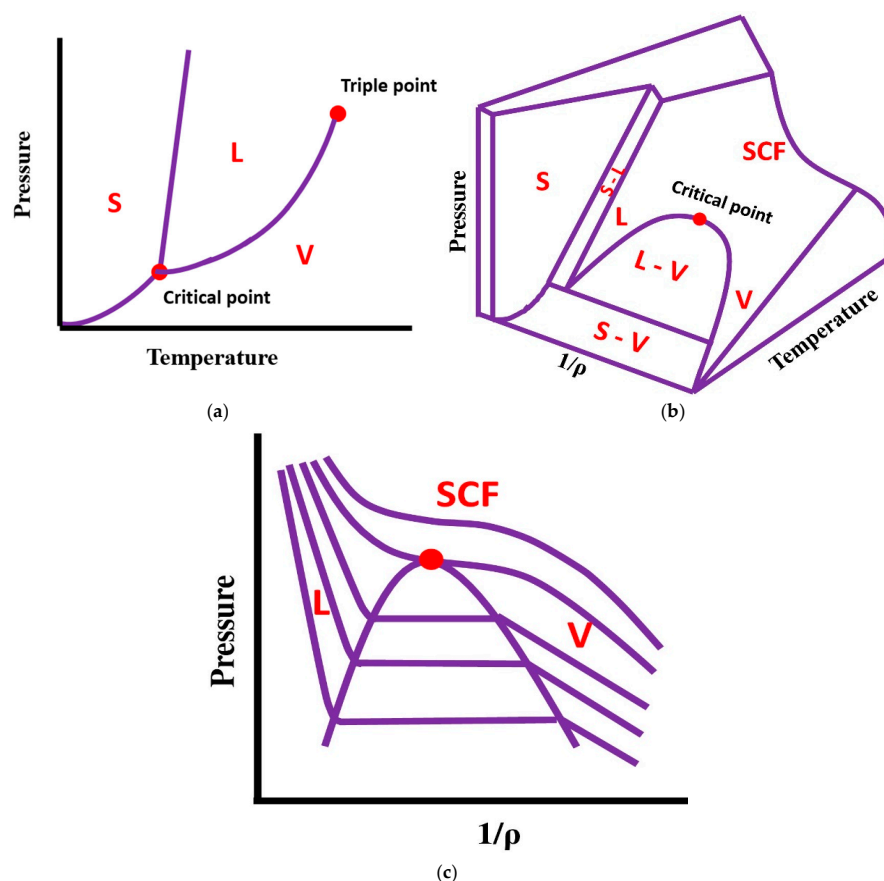


Figure 5. Pure CO₂ state surface [6]. (a) P–T phase diagram. (b) Three-dimensional phase diagram. (c) P–1/ρ phase diagram.

3. Experimental Methodologies

3.1. Overview of High-Pressure Phase Equilibrium

Understanding phase equilibria is essential for high-pressure process analysis, design, and optimization, contributing to cost reduction, environmental protection, and operational safety [7]. Pressure strongly governs thermodynamic equilibrium, phase coexistence, and composition. In CO₂-based systems, the solubility of most compounds in liquid or SC-CO₂ is limited, while the vapour pressure of CO₂ at room temperature exceeds 6 MPa [4], requiring elevated pressures to achieve even modest solute concentrations [41]. High-pressure conditions favour volume-reducing phase transitions and generally enhance solubility, for example, by increasing the solubility of liquids and solids in dense supercritical fluids or gases in liquids and polymer matrices, while also reducing density contrasts between coexisting phases [42]. Continued interest in supercritical fluid technologies sustains intensive research into high-pressure phase equilibria [43].

Despite the availability of various methodologies, direct experimental measurement of phase equilibrium data remains indispensable, despite its complexity and cost [44], as inaccurate or repeatedly estimated data are often more expensive in the long term. Comprehensive reviews have addressed high-pressure equilibrium data [45,46] and experimental techniques for fluid phase behaviour [47].

3.2. Classification of High-Pressure Phase Equilibrium Experimental Methodologies for CO₂ Systems

For CO₂-containing mixtures, accurate phase equilibrium determination is particularly critical due to strong non-ideality, high compressibility, and near-critical density sensitivity. Accordingly, predictive thermodynamic models rely heavily on high-quality experimental

data for vapour–liquid (VLE), liquid–liquid (LLE), and critical phenomena, and experimental methods are commonly classified by whether phase compositions are measured analytically or inferred from known overall compositions, with method selection governed by CO₂ volatility, depressurization-induced density changes, and near-critical effects. This chapter presents both an outline and a classification of experimental techniques utilized in discerning high-pressure phase equilibria as proposed by Dohrn et al. [43,47,48].

Experimental techniques for high-pressure phase equilibrium measurements are commonly classified according to whether phase compositions are determined analytically or inferred from known overall compositions. Hence, there are two categories of experimental methods, namely, analytical methods and synthetic methods, as shown in Figure 6. In the context of CO₂ systems, method selection is strongly influenced by factors such as CO₂ volatility, density changes upon depressurization, and the presence of near-critical phenomena.

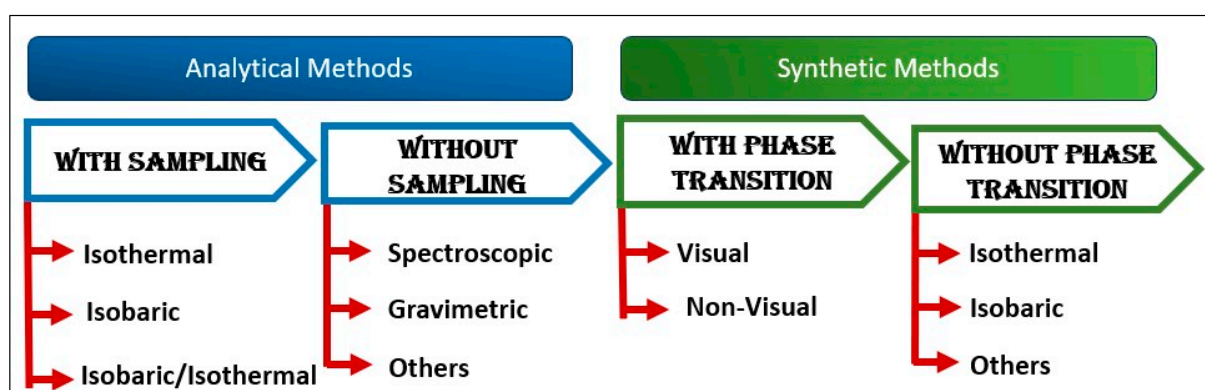


Figure 6. Classification of high-pressure experimental methods for phase equilibria [48].

3.2.1. Analytical Methods

Analytical methods determine the compositions of coexisting phases through direct chemical or physicochemical analysis and are central to high-pressure phase equilibrium studies. For CO₂-containing systems, accurate data are particularly important due to strong non-ideality, high compressibility, and pronounced density sensitivity near the critical region; consequently, predictive thermodynamic models rely heavily on high-quality experimental measurements of vapour–liquid (VLE), liquid–liquid (LLE), and critical equilibria.

These methods are broadly classified into sampling and non-sampling techniques, depending on whether phase compositions are analyzed ex situ or in situ (Figure 6). Sampling-based methods involve withdrawing samples from coexisting phases in a high-pressure equilibrium cell and are further subdivided into isothermal, isobaric, and isothermal–isobaric techniques (Figure 6). Their principal limitation is disturbance of equilibrium during depressurization, which can alter phase compositions and compromise sample representativeness [49,50]. To minimize these effects, we can use syringe pumps and buffer autoclaves [51], incorporate a variable volume cell [52], isolate the remaining content in the cell from the sampling volume [53], or withdraw a small sample or utilize a relatively larger equilibrium cell [48].

Isothermal methods are widely used for CO₂ VLE measurements, where equilibrium is achieved at constant temperature and pressure adjusts according to system composition and cell volume [7]. However, sampling-induced pressure drops may trigger re-equilibration, requiring careful mitigation [54]. Isobaric methods, typically using ebulliometers, determine phase compositions at constant pressure and are mainly applied at low to moderate pressures, with some high-pressure extensions reported [44,48,55]. Isothermal/isobaric

methods including semi-flow, continuous-flow, and chromatographic techniques, are particularly suitable for CO₂ systems at elevated pressures, offering continuous operation and improved reproducibility [7,48]. In these approaches, controlled fluid streams are introduced into temperature-regulated equilibrium cells and phase compositions are determined from depressurized effluents [56–58]. Chromatographic methods additionally provide access to equilibrium and transport properties via solute retention behaviour [59].

Non-sampling analytical methods are especially advantageous for CO₂ systems, as they avoid depressurization artefacts and enable in situ measurements under true equilibrium conditions (Figure 6). Spectroscopic techniques such as NMR [60], FTIR, UV-Vis [61], X-ray scattering [62], Raman [63] and infrared spectroscopy [64] allow for rapid analysis of phase compositions and molecular interactions, though extensive calibration may be required. Gravimetric methods determine phase compositions from the mass of a condensed phase in equilibrium with a fluid phase [65,66], with buoyancy corrections relying on accurate density data [67,68]. Additional techniques, including quartz crystal microbalance methods [64–66], palladium-based hydrogen sensors [69], and capacitive techniques for low-volatility solutes [70], have also been applied to CO₂-containing systems.

3.2.2. Synthetic Methods

Synthetic methods determine phase behaviour by preparing mixtures of known overall composition and monitoring equilibrium properties such as pressure, temperature, or volume, thereby eliminating the need for phase sampling. These methods are particularly well-suited for CO₂-containing binary systems, where sampling of CO₂-rich phases is difficult due to rapid expansion and density changes upon depressurization. Compared with analytical methods, synthetic approaches require simpler experimental setups and preserve equilibrium conditions, although they provide limited compositional information and are therefore mainly applied to binary systems.

Synthetic methods may be employed with or without phase transition detection. In phase-transition-based approaches, pressure or temperature is varied until the appearance of a new phase is detected, enabling determination of cloud points, bubble points, dew points, and critical points in CO₂ mixtures, especially near the critical region. Such methods are classified as visual or non-visual. Visual synthetic methods use variable-volume view cells with transparent windows to detect turbidity or meniscus formation and have been widely applied to VLE, solid–liquid equilibria [71], multiphase equilibria [72], gas hydrate formation [73], phase equilibria in polymer–solvent systems [74], cloud point determinations of mixtures of monomers in SC-CO₂ [75–80], phase equilibria of polymer–solvents in SC-CO₂ [81–83], etc. Extensive CO₂ phase equilibrium data obtained using visual synthetic methods have been reported by Byun’s group employing variable-volume view cells [84,85].

Non-visual synthetic methods detect phase transitions through changes in physical properties such as pressure–volume behaviour [86,87], dielectric permittivity [88], ultrasonic or acoustic signals [89,90], and calorimetric responses [91], and are particularly useful when optical access is limited. Synthetic methods without phase transition, most notably the isothermal pressure-decay method, are widely used to measure CO₂ solubility in liquids, polymers, and ionic liquids by exploiting the high compressibility of CO₂ [92]. Additional non-transition approaches include quasi-static thermogram techniques, isothermal microcalorimetry [93], two-phase isochoric heat-capacity measurements [94], and isochoric PVTx measurements combined with equation-of-state modelling [95].

3.2.3. Method Selection for CO₂-Based Systems

The choice of experimental methodology for CO₂ phase equilibrium studies depends on the target properties (solubility, critical points, tie-lines), the pressure–temperature range, and the nature of the second component. Near-critical CO₂ systems often require techniques capable of handling strong density fluctuations and minimizing disturbances to equilibrium.

In practice, a combination of synthetic and analytical methods is frequently employed to obtain comprehensive and reliable datasets. Given the central role of CO₂ in supercritical technology and carbon capture applications, continued development and refinement of CO₂-specific experimental methodologies remain essential for advancing both fundamental understanding and industrial implementation.

4. Phase Behaviour of Binary Systems

4.1. Description of Phase Diagrams

Phase diagrams play a pivotal role in elucidating the complex interplay of thermodynamic variables governing the phase behaviour of materials. Examining binary mixtures is valuable in comprehending the behaviour of multicomponent mixtures, as it provides insight into the interactions between unlike molecules. Due to the diverse range of observed phase behaviour in practical applications, it becomes useful to categorize various types of phase diagrams. The classification scheme in [96,97] has been established by Van Konynenburg and Scott by analyzing the critical equilibria behaviour of binary mixtures. Fluid phase behaviour is organized into six distinct types, as illustrated in Figure 7. It is important to note that the depicted phase diagrams do not portray real experimental data or calculations; rather, they serve as schematic representations to illustrate the different behavioural types.

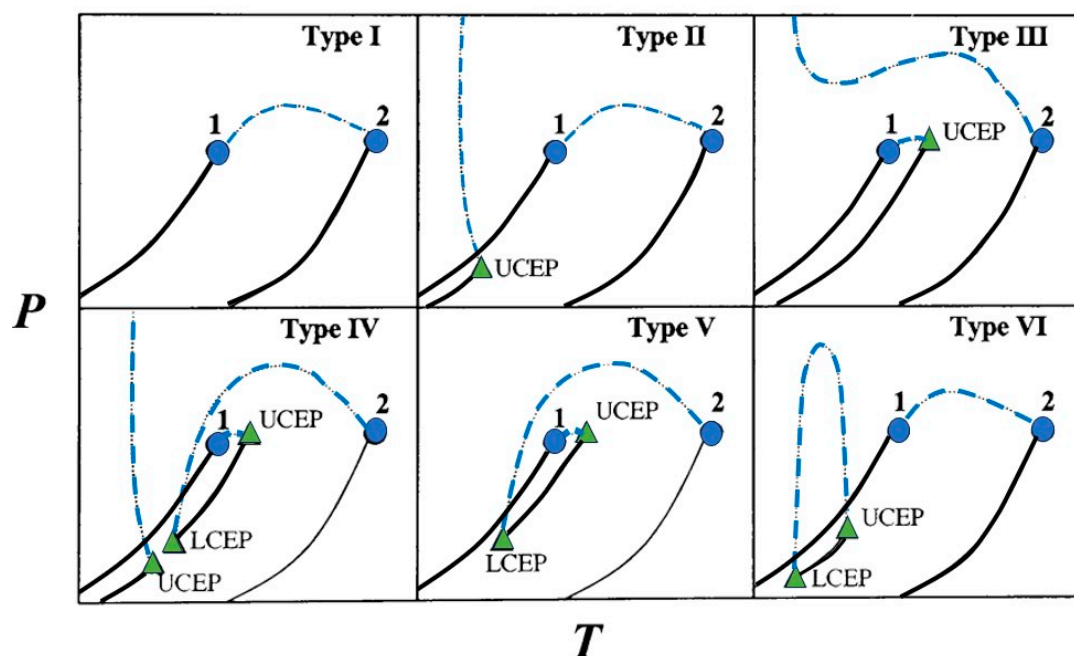


Figure 7. PT projections of the phase behaviour diagram for binary mixtures. The continuous curves are pure components vapour pressure curves (1 and 2) and three phase lines. The dashed curves are critical lines. The upper and lower end critical points are represented by filled triangles. The critical points of pure components are denoted by filled circles. The figure is reproduced with permission from reference [98].

Type I and Type II fluids exhibit strikingly comparable behaviour. In both instances, a continuous critical line is evident, connecting the critical point of the individual pure components. Type I diagram is commonly observed when the two components of the mixture possess critical properties of comparable magnitude or exhibit similar molecular sizes and interaction energies [99]. Type I behaviour is, for example, observed for mixtures of CO₂ + short alkanes. For Type II mixtures a liquid–liquid immiscibility region appears at low temperatures and extends to high pressures. A corresponding liquid–liquid–gas three-phase line is observed in this low-temperature range, terminating at the upper critical end point (UCEP). This liquid–liquid immiscibility region is often caused by unfavourable cross-interactions between unlike molecules compared with the interactions between like molecules. For example, Type II behaviour is observed for mixtures of linear alkanes with CO₂, such as CO₂ + n-C₁₂, where the appearance of an LLE region is attributed to the large quadrupole moment of the CO₂ molecule.

For Type III fluids, the critical line originates from the pure component with the higher critical point (2) and extends towards the critical point of the other component (1). However, it sharply deviates from the critical point of component 1, while the vapour–liquid phase changes to liquid–liquid at high pressure. Additionally, another critical line is observed between the critical point of component 1 and the upper critical end point (UCEP). Type III phase behaviour is observed for highly non-ideal mixtures for which cross interactions are strongly unfavourable, such as in the methane + water mixture. Type III is also observed for very asymmetric systems, such as CO₂ + very long linear alkanes (CO₂ + n-tetradecane for example). In Type IV mixtures, the critical line originating from component 2 (higher critical temperature) terminates at the lower critical end point (LCEP), while the critical line from component 1 ends at the upper critical end point (UCEP). At low temperatures, the three-phase (liquid–liquid–gas) line terminates at the UCEP, from which a liquid–liquid immiscibility region extends and expands rapidly at higher pressures. Type IV behaviour represents a transitional case between Types II and III, observed, for example, when mixing CO₂ with linear alkanes of progressively longer chain length: CO₂ + n-C₁₂ is of type II, CO₂ + n-C₁₃ is of type IV and CO₂ + n-C₁₄ is of type III. The transition occurs such that the two liquid–liquid critical lines observed in Type IV merge, leading to Type III phase behaviour. The phase behaviour of Type IV and Type V fluids is comparable, except for the absence of the liquid–liquid immiscibility region at low temperature that ends at a UCEP. Type IV and V phase behaviour typically manifest when the critical properties of the two components exhibit significant differences, often attributed to variations in molecular size, structure, or intermolecular forces [100]. For Type VI fluids, a continuous critical line connects the critical points of components 1 and 2, similar to Type I and II. Type VI behaviour is characterized by a liquid–liquid immiscibility line that ascends from the UCEP and descends at the LCEP, or vice versa. Type VI phase behaviour can be observed in binary mixtures with cross hydrogen bonding interactions, such as in the water + butan-2-ol mixture. Coquelet et al. [101] visually illustrate the transition between each type of phase behaviour (Type I to Type VI) in Figure 8. The potential shifts between these behaviours are depicted based on the size and molecular interaction effects between molecules.

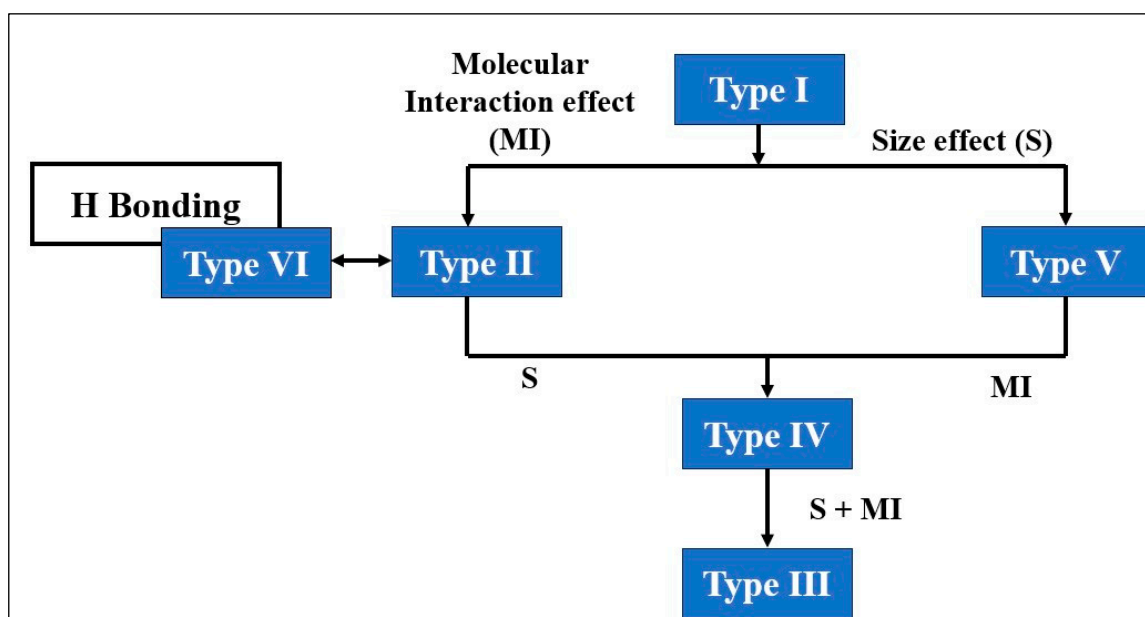


Figure 8. The transitions between different types of phase diagrams [101].

4.2. Review of Phase Equilibrium Studies in Mixtures Involving CO₂

In this segment of our investigation, we delved into a comprehensive thermodynamic exploration of binary systems involving CO₂ and examined interactions of CO₂ with a diverse range of chemical functionalities, encompassing aliphatic and aromatic hydrocarbons, alcohols, ethers, esters, ketones, water, monomer/polymer systems, ionic liquids, and deep eutectic solvents. A broad variety of experimental data for binary systems involving CO₂, including solubilities, bubble and dew pressures or temperatures, and gas–liquid critical points, is provided in the Supplementary Materials (Tables S2–S11). These data are crucial in optimizing various applications involving CO₂. For instance, in separation processes, a thorough understanding of phase behaviour allows for the targeted extraction of desired components from a mixture. It can also lead to the development of novel materials with tailored properties. Ultimately, the insights gleaned from this investigation pave the way for the broader utilization of SC-CO₂ as a sustainable and versatile tool across a range of scientific and industrial applications.

Recent decades have witnessed a surge in research dedicated to unravelling the intricacies of CO₂ interactions with organic and inorganic compounds [102,103]. Traditionally, the focus was on CO₂ acting as a proton acceptor, forming hydrogen bonds with various molecules. However, a more comprehensive picture has emerged, revealing the adaptability of CO₂ in its electron behaviour. Depending on the interacting molecule, CO₂ can act as an electron acceptor (Lewis acid), an electron donor (Lewis base), or retain its proton-accepting role. The Lewis acid–base theory provides a valuable framework for understanding this versatility. This perspective posits that CO₂ can act as a solvent for a range of dipolar and nonpolar molecular systems due to site-specific interactions between the solute and the solvent. CO₂'s partially positive carbon atom can act as an electrophilic centre due to the electron-withdrawing nature of the oxygen atoms. This allows it to form electron donor–acceptor complexes with Lewis bases, molecules possessing electron-rich lone pairs. Common examples of Lewis bases that readily interact with CO₂ through this mechanism include water, alcohols (like methanol and ethanol), ketones, amines, and amides. These interactions highlight CO₂'s ability to participate in electron transfer processes, expanding its role beyond the traditional view of solely acting as a hydrogen bond acceptor. This newfound understanding of CO₂'s diverse interaction modes is crucial for various scientific

fields. It has implications for CO₂ capture and utilization technologies, where the nature of interactions with capture agents directly impacts efficiency. Additionally, it informs the development of accurate models describing CO₂-molecule interactions at a molecular level, which is essential for advancing fields like catalysis and material design.

Solubilization or solute dissolving in a solvent can be broken down into two key thermodynamic steps, as shown in Figure 9 [104]. Firstly, cavities are formed within the solvent (red circles) that are large enough to accommodate the solute molecules (yellow circles). This cavity creation disrupts existing solvent–solvent interactions, requiring energy input. Secondly, the solute molecules are incorporated into these cavities. This step is typically exothermic, releasing energy due to the formation of new solute–solvent interactions. The effectiveness of a solvent in dissolving a solute is determined by the overall energy balance of these two steps. A good solvent minimizes the energy required for cavity creation while maximizing the energy released during solute interaction.

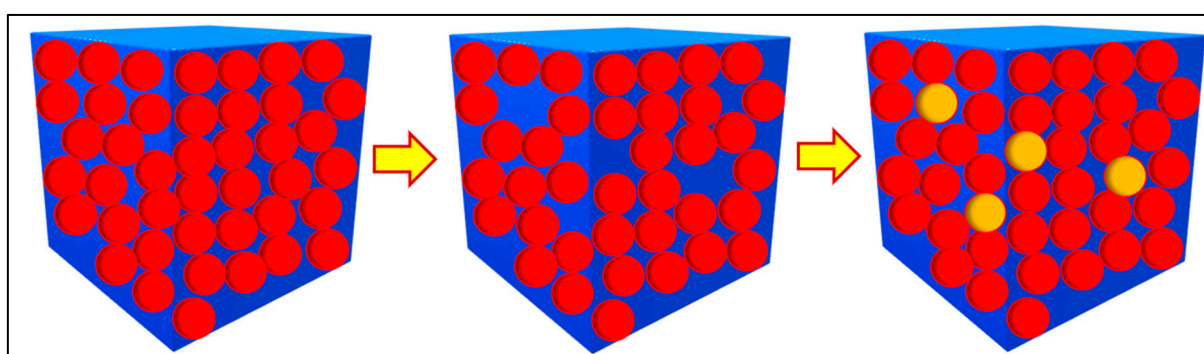


Figure 9. Thermodynamic steps of solubilization of solute in solvent [104].

4.2.1. Aliphatic Hydrocarbon/CO₂ Binary Systems

The investigation of the solubility of different hydrocarbons in CO₂ is crucial in contexts such as separation processes (separating lighter hydrocarbons from heavier one in natural gas streams), enhanced oil recovery, fractionalization in refining processes, etc. In a study by Dandge et al. [105], short-chain alkanes (up to C₁₂) were completely miscible with CO₂. However, longer alkanes showed a sharp decrease in solubility with increasing chain length. Experimental VLE and LLE solubility data for binary mixtures of aliphatic hydrocarbons in SC-CO₂ are covered in the Supplementary Materials (Table S2). The solubility of n-alkanes in CO₂ is directly related to the density of CO₂. As the density of CO₂ increases, the solvent strength of the supercritical fluid also increases at a constant temperature. This means that higher CO₂ density enhances the ability of CO₂ to dissolve n-alkanes.

It is observed that higher pressure enhances the solubility of n-alkanes in SC-CO₂. On the other hand, when the pressure is held constant and the temperature is increased, the solubility of n-alkanes in SC-CO₂ decreases. As the temperature increases, the bubble point pressure of C₁₀H₂₂ in SC-CO₂ also increases, as demonstrated in Figure 10. This can be explained with the fact that P-x phase diagrams at fixed temperature in binary systems are shifted to higher pressures when temperature is increased. In terms of solvation, this can be explained by the fact that the solvent (CO₂) density decreases at a higher temperature, lowering the effective attractions between solvent and alkane molecules. Therefore, a higher pressure is required at a higher temperature to get the same alkane solubility in CO₂.

The length of the alkane chain also significantly affects the bubble point pressure in SC-CO₂. As the chain length of n-alkanes increases, the bubble point pressure also increases, as illustrated in Figure 11, meaning that longer alkanes are less soluble in SC-CO₂. As shown by Blas and Galindo [106], there is a continuous change from type II

to type III phase behaviour (going through type IV) as the chain length of the n-alkane increases. Paricaud et al. [107] provided a detailed explanation for the enlargement of the immiscibility region for asymmetric binary mixtures as the chain length difference between the two compounds increases. Kobayashi et al. [108] mentioned that molecular engineering is a potential approach for improved CO₂-philicity and hence solubility in CO₂. The influence of molecular architecture on solubility in SC-CO₂ has been extensively investigated [109,110]. Studies have consistently demonstrated that branched alkanes exhibit enhanced solubility in SC-CO₂ compared to their n-alkane counterparts with similar molecular weights. This phenomenon can be attributed to the disruption of close packing in n-alkanes by the steric hindrance introduced by methyl branches in branched alkanes. The resulting increase in free volume within the branched alkane structure facilitates favourable interactions with SC-CO₂ molecules, ultimately leading to higher solubility.

In a study by Shi et al. [111], the influence of system conditions (pressure and temperature) and solution properties (CO₂ density and n-alkane chain length) on the solubility of n-alkanes (C₉–C₃₆) was investigated. Their findings revealed a direct correlation between n-alkane solubility and both CO₂ density and system pressure.

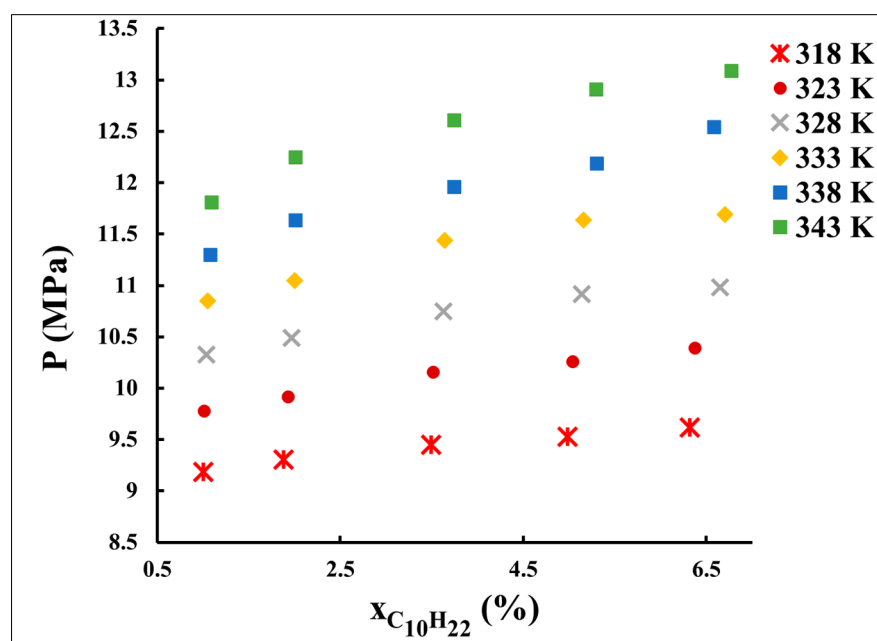


Figure 10. Experimental pressure vs. solubility curves of C₁₀H₂₂ in SC-CO₂ at different temperatures. Experimental data is taken from Ref. [111].

4.2.2. Aromatic Hydrocarbon/CO₂ Binary Systems

The effects of changing temperature and pressure on the solvation behaviour of aromatic hydrocarbons in CO₂ were extensively studied, as shown in the Supplementary Materials (Table S3). One can observe that the solvation of aromatic hydrocarbons by CO₂ became less important at higher temperatures. Moreover, the high-pressure environment promoted the solvation behaviour of aromatic hydrocarbons in CO₂, as shown in Figure 12 for mixtures of benzene and toluene in CO₂. As per the study by Rizvi et al. [112], small aromatic hydrocarbons are soluble in SC-CO₂. Schroeder concluded that, in general, aromatic compounds tend to have lower solubility compared to their hydrogenated counterparts [113]. Hydrogenation of an aromatic compound results in a molecule that has the same basic structure as the original compound, but some of its double bonds have been replaced by single bonds with hydrogens attached. This addition of hydrogens typically

decreases the molecule's overall polarity, e.g., cyclohexane is the hydrogenated counterpart of benzene.

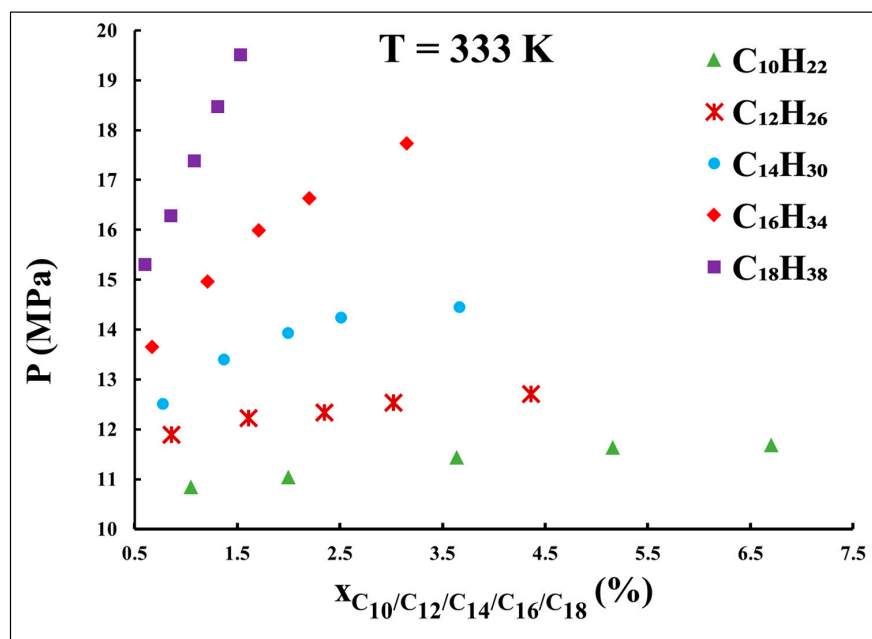


Figure 11. Experimental pressure vs. solubility plot for hydrocarbons in SC-CO₂ at T = 333 K. Experimental data is taken from Ref. [111].

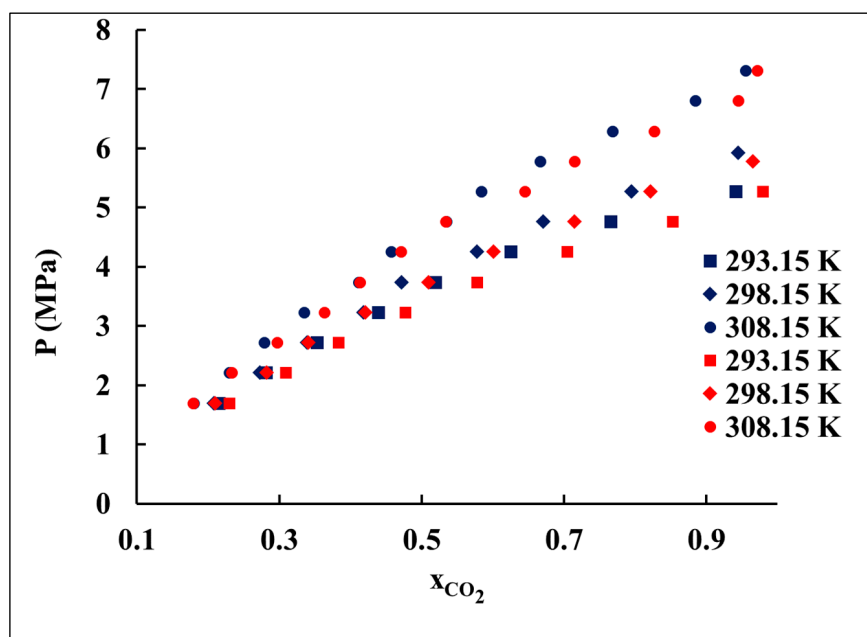


Figure 12. Experimental bubble pressure vs. liquid phase mole fractions CO₂ + aromatic binary systems at various temperatures. Red symbols denote Benzene + CO₂ and purple symbols denote Toluene + CO₂. Experimental data are taken from Ref. [114].

4.2.3. Alcohol/CO₂ Binary Systems

Studies suggest that the relationship between alcohol chain length and solubility in CO₂ is complex. Experimental VLE data of CO₂ and alcohol binary systems are reported in the Supplementary Materials (Table S4). Gauter et al. [115] investigated the phase behaviour of CO₂/alcohol systems. Their findings indicate that, based on the classification scheme

established by Van and Scott [97], the majority of these alcohol-containing systems exhibit Type III or Type IV behaviour.

Shorter-chain alcohols (up to C₆) are completely miscible with CO₂ [105,112]. Solubility then drops sharply for longer-chain alcohols as the hydrophobic hydrocarbon chain disrupts interactions with CO₂. Fourie et al. [116] have discussed the effect of hydroxyl group position on the solubility of C₈ alcohol. The key findings of the authors are as follows: (1) The position of the hydroxyl group directly influences solubility; 1-Octanol, which has the hydroxyl group at the first carbon atom, possesses the largest polarity and lowest solubility among the studied alcohols. (2) Shifting the hydroxyl group from the first to the second carbon atom causes a large decrease in polarity and an increase in solubility. (3) Further movements of the hydroxyl group towards the molecule centre result in progressively smaller reductions in polarity and increases in solubility. (4) The non-terminal octanol molecules (2-Octanol, 3-Octanol, and 4-Octanol) exhibit similar behaviour with smaller polarities and much higher solubilities compared to 1-Octanol. (5) 1-Octanol exhibits a broad range of phase transition pressures due to its high dependence on bulk composition, which is believed to be a result of the large difference in polarity between 1-octanol and carbon dioxide. (6) Only at higher temperatures do 2-Octanol, 3-Octanol, and 4-Octanol develop marginal differences in phase transition pressure. (7) Temperature influences the pressure at phase transition (i.e., solubility) for the studied alcohols. An increase in temperature is accompanied by a decrease in solubility and a subsequent increase in phase transition pressure. (8) The difference in solubility pressure between 1-Octanol and the non-terminal octanols decreases with an increase in temperature.

Reilly et al. [117] challenge the traditional view of liquid CO₂ interacting with methanol solely through hydrogen bonding. Their proposition suggests that CO₂ acts as a Lewis acid in this interaction. This Lewis acid–base interaction might play a more significant role than previously thought. The reasoning behind this proposal involves techniques to analyze the interaction between CO₂ and methanol, through Fourier Transform Infrared spectroscopy. In another study by Liu et al. [118], the key focus was to study the solubility behaviour of alcohols and alkanes in SC-CO₂. The oxygen atom in an alcohol (R-OH) is sp³-hybridized. sp³ hybridization leads to better electron donation compared to sp²/sp hybridization. And hence, it is expected that the oxygen atom in an alcohol participates in Lewis acid–base interactions with CO₂ [119]. In general, higher pressures in SC-CO₂ systems tend to enhance the solubility of alcohols and alkanes. This phenomenon is particularly pronounced in the near-critical and supercritical regions of the system. As pressure increases, the density of the supercritical fluid also increases, leading to improved solvation and interaction between the solvent (SC-CO₂) and the solutes (alcohols and alkanes).

The solubility isotherms of 1-Butanol and 1-Octanol in SC-CO₂ are shown in Figure 13. Comparing the two, 1-Butanol, with its shorter alkyl chain and stronger hydrogen bonding, exhibits higher solubility at a given pressure (or a lower critical pressure). In contrast, 1-Octanol, due to its longer alkyl chain, experiences stronger van der Waals interactions and Lewis base interactions with CO₂, leading to higher peak pressures but lower solubility relative to 1-Butanol at equivalent pressures. The pressure-composition phase diagram of the undecan-2-ol + CO₂ mixture is shown in Figure 14. CO₂ solubility in alcohols have been investigated by several authors [120–123]. It is observed that CO₂ solubility in alcohols increases with pressure and decreases with temperature.

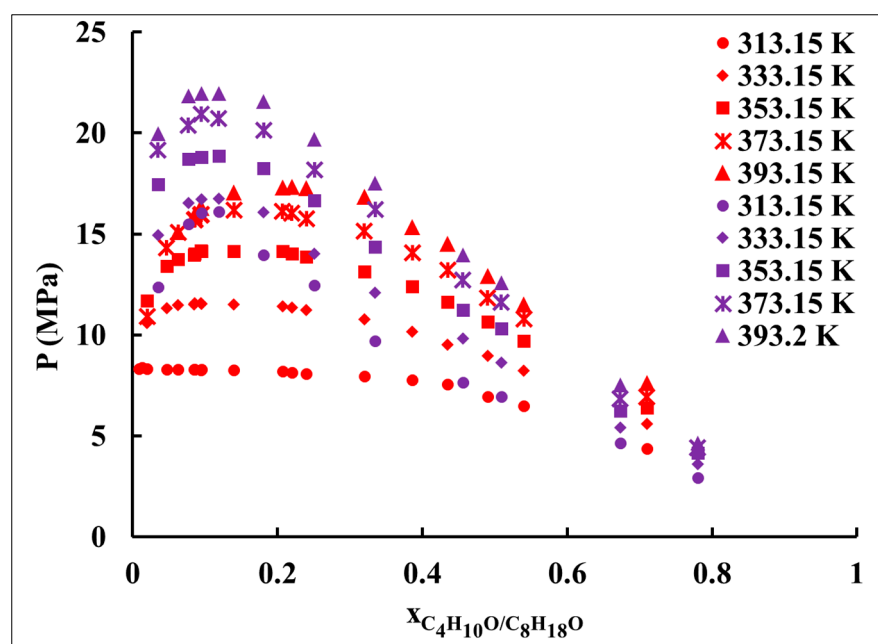


Figure 13. Experimental isotherms for 1-Butanol/ CO_2 (Red symbols) and 1-Octanol/ CO_2 (purple symbols). The experimental data is taken from Ref. [124].

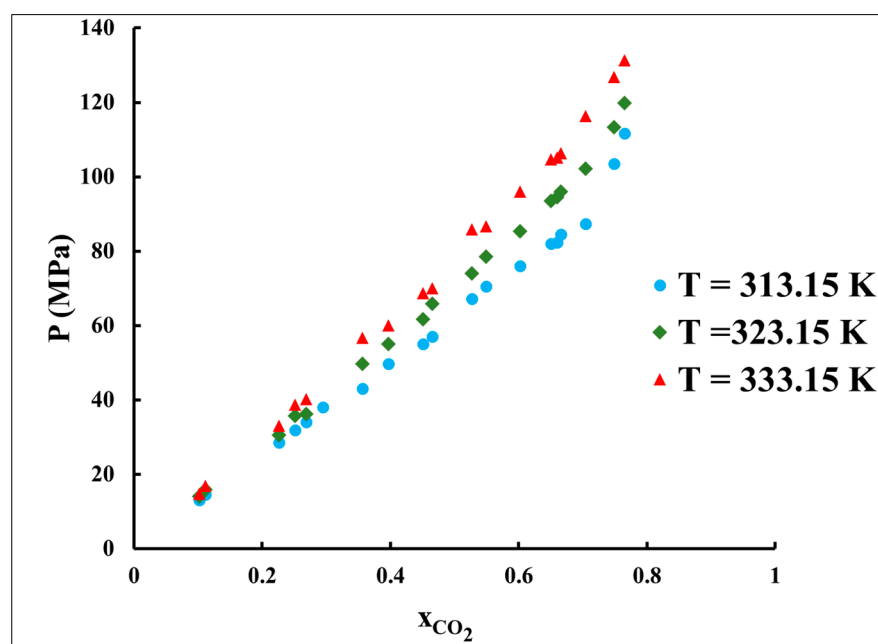


Figure 14. Experimental isotherms for CO_2 in undecan-2-ol. The experimental data is taken from Ref. [125].

4.2.4. Ether/ CO_2 , Ester/ CO_2 , and Ketone/ CO_2 Binary Systems

Experimental studies have been conducted to investigate the solubility of ethers in CO_2 and the impact of different parameters such as pressure, temperature, and cosolvent composition on their solubility behaviour, as illustrated in the Supplementary Materials (Table S5). Ethers, being nonpolar compounds, typically exhibit limited solubility in CO_2 due to the nonpolar nature of both the solvent and the solute. The addition of cosolvent modifiers or entrainers can enhance the solubility of ethers in CO_2 by promoting interactions between the ether molecules and the CO_2 solvent. The chemical structure of ethers, including the length of alkyl chains and the presence of functional groups, plays a significant role in determining their solubility in CO_2 . Ethers with longer alkyl chains may

have higher solubility in SC-CO₂ due to increased van der Waals interactions between the molecules [113].

The insights into the solubility of esters and ketones in carbon dioxide can be obtained by analyzing the Supplementary Materials (Tables S6 and S7), respectively. The chemical structure of esters, including the length of carbon chains, the presence of functional groups like ester groups, and the degree of polarity, impact their solubility in CO₂. Ester molecules with longer carbon chains or more polar functional groups have different solubility behaviour in SC-CO₂ compared to shorter-chain esters or less polar compounds. Ethers, esters, and ketones extraction can be carried out at a lower range of pressures, i.e., 7–10 MPa [20,113]. Carbonyl compounds such as ketones and esters have high solubility in SC-CO₂ [112]. The Lewis acid–base interaction between the carbonyl group (Lewis base) and SC-CO₂ (Lewis acid) is crucial for the high solubility of carbonyl-containing compounds in SC-CO₂. There is an attractive force between the partial positive charge on the carbon of SC-CO₂ and the lone pair electrons on the oxygen of the carbonyl group. This interaction leads to the formation of a weak bond between the carbonyl compound and SC-CO₂ molecules, promoting the dissolving of the carbonyl compound in SC-CO₂ [126,127]. Kazarian et al. [128] have confirmed this interaction between carbonyl-containing compounds and SC-CO₂ using IR spectroscopy. Ethers, on the other hand, have sp³-hybridized oxygen atoms. The propensity for sp³-hybridized oxygen atoms to act as Lewis bases surpasses that of their sp² counterparts. This observation suggests that the oxygen atoms in ethers (R-O-R') and alcohols (R-OH) can potentially engage in Lewis acid–Lewis base (LA-LB) interactions with CO₂, akin to the behaviour observed with carbonyl groups.

The study by Altarsha et al. [129] suggests that the stability of complexes where carbon dioxide behaves as a Lewis base in the case of ketones and esters is comparable to that of traditional complexes where CO₂ acts as a Lewis acid. The study, based on ab initio calculations, reveals that complexes where CO₂ behaves as a Lewis base are stable in the case of ketones and esters. These findings challenge conventional notions of CO₂-philicity and have implications for understanding the solubility of carbonyl compounds in SC-CO₂. The results indicate that these non-conventional structures may play a significant role in the solubility of ketones and esters in SC-CO₂, potentially impacting the development of green reactions in this medium. Kajiya et al. [130] have investigated the solvation behaviour of ketones and esters in SC-CO₂. The findings of the study are expected to be useful for various applications of SC-CO₂, such as in polymers, biomolecules, and pharmaceutical agents. The vibrational Raman spectra of esters and ketones in SC-CO₂ showed common shifts to lower energy as the CO₂ density increased. The energy shifts were decomposed into attractive and repulsive energies using the perturbed hard-sphere theory. It was found that the attractive energies were always greater than the repulsive energies for all six carbonyl compounds studied.

Based on the observations by Gwinner et al. [104], the most favourable solvent families for CO₂ absorption are ethers, esters, and ketones. Regarding CO₂ solubility in ethers, investigations into CO₂ solubility across various absorbents revealed that the presence of a carbonyl group (C=O) or an ether linkage (C-O-C) within the solvent molecule facilitated CO₂ uptake [120]. Conversely, the presence of a hydroxyl group (O-H) hindered CO₂ absorption. More specifically ketones exhibit a superior capacity for CO₂ dissolution compared to alcohols, ethers, and glycols [120]. This can be attributed to the differing abilities of these functional groups to engage in intermolecular interactions with CO₂. Carbonyl groups can participate in Lewis acid–base reactions with CO₂, while ether linkages can induce dipole–dipole attractions. In contrast, hydroxyl groups tend to form stronger hydrogen bonds with themselves through intramolecular interactions, reducing the available sites for interaction with CO₂ molecules. CO₂ solubility exhibits a positive correlation with

carbon chain length. The increasing length of a solvent's carbon chain can influence its CO₂ capture ability. As the chain lengthens, London dispersion forces between solvent molecules weaken. This weakening is due to a diminishing effect on overall polarizability compared to the increased separation caused by additional methylene groups. Furthermore, the larger size of the solvent molecule with a longer chain creates bigger cavities when the solvent structure fluctuates. These larger cavities can more readily accommodate CO₂ molecules, leading to enhanced CO₂ solubility in the solvent.

Figure 15 illustrates the experimental pressure vs. solubility isotherms of a CO₂/dimethyl ether mixture at different temperatures. The solubility decreases with increasing temperature, requiring higher pressures to dissolve the same amount of dimethyl ether at higher temperatures. The relationship between pressure and mole fraction of dimethyl ether is consistent across all temperatures, but the required pressures increase with temperature, reflecting the typical solubility behaviour of gases in liquids. Figure 16, on the other hand, demonstrates solubility isotherms of propyl oleate in CO₂. It is observed that, for a given temperature, as the mole fraction of propyl oleate increases, the pressure generally decreases. At higher temperatures, the isotherms shift to higher pressures for the same mole fraction of propyl oleate. This suggests that at higher temperatures, a higher pressure is required to dissolve the same amount of propyl oleate in CO₂. The decreasing pressure with increasing mole fraction at a constant temperature suggests favourable interactions between CO₂ and propyl oleate, leading to good solubility. Experimental pressure vs. solubility isotherms of CO₂ in acetone mixture are shown in Figure 17. As illustrated above, the graph shows the typical solubility behaviour of gases in liquids.

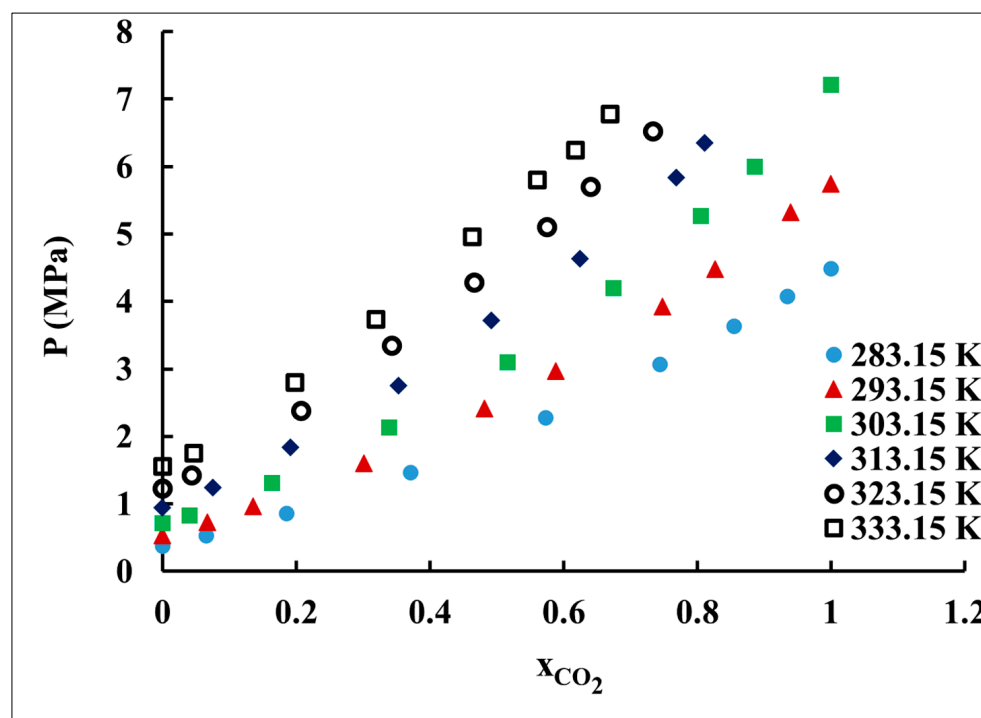


Figure 15. Experimental pressure vs. solubility isotherms of dimethyl ether/CO₂ mixture. Experimental data is taken from Ref. [131].

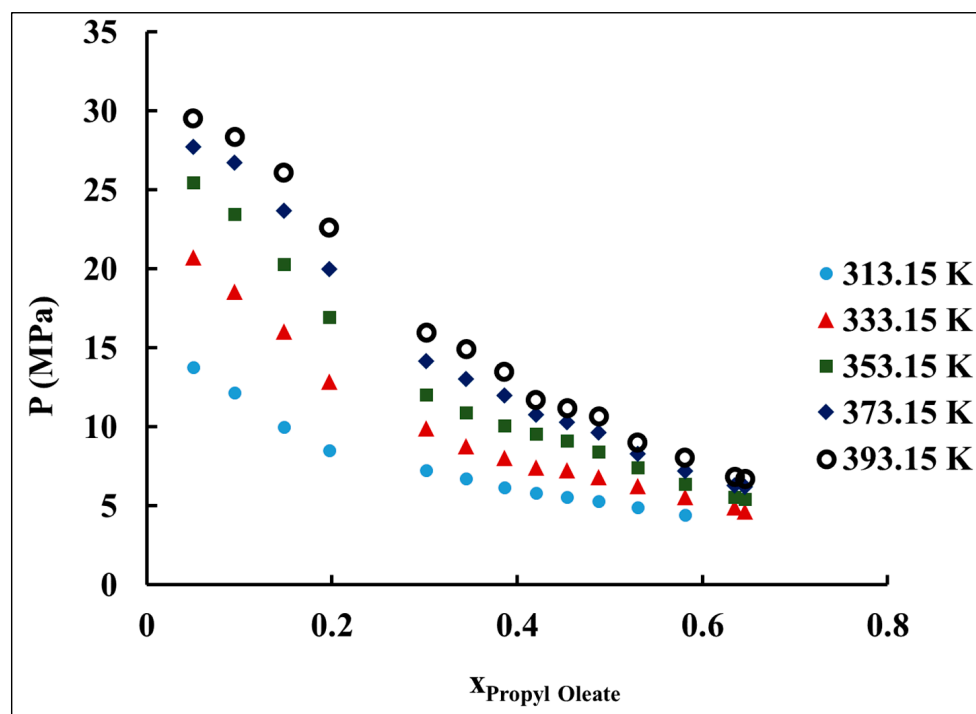


Figure 16. Experimental pressure vs. composition isotherms of propyl oleate/ CO_2 mixture. x : mole fraction of propyl oleate. Experimental data is taken from Ref. [132].

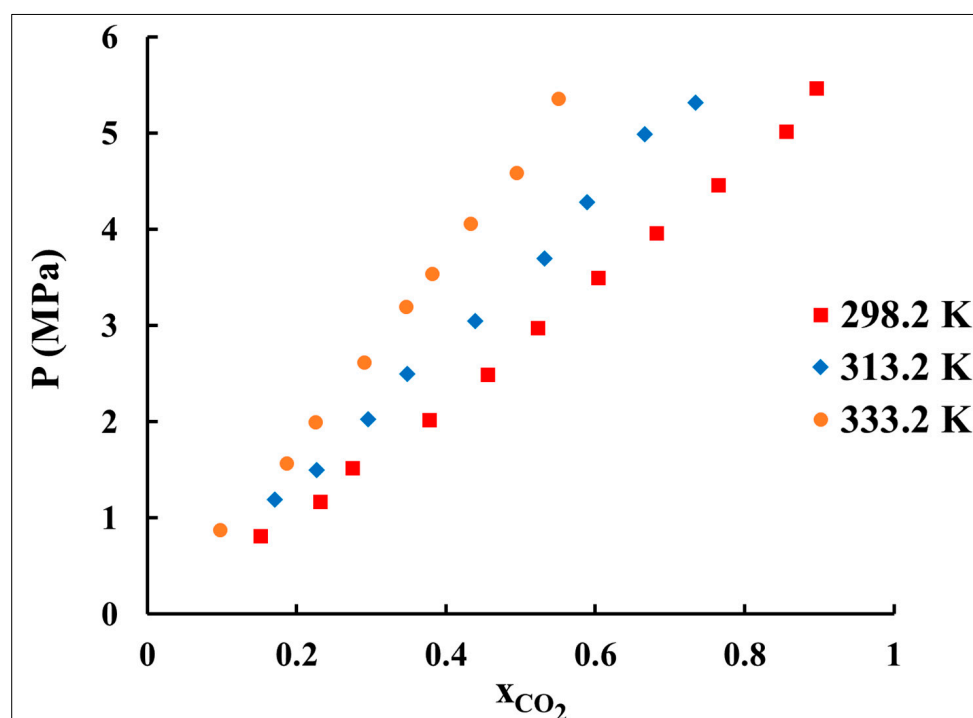


Figure 17. Experimental pressure vs. composition isotherms of acetone/ CO_2 mixture. Experimental data is taken from Ref. [133].

4.2.5. Water/ CO_2 Binary System

Several industrial applications, including CO_2 -enhanced oil recovery (EOR), CO_2 sequestration in saline formations and depleted hydrocarbon reservoirs, geological storage of CO_2 and the treatment of industrial wastewater contaminated with dissolved acid gases, necessitate a thorough understanding of the CO_2 - H_2O system's thermodynamic behaviour. The dissolution of CO_2 in water at moderate pressures (less than 10 MPa) readily yields

carbonic acid (H_2CO_3), leading to a decrease in solution pH [4]. This acidic environment presents a significant obstacle in biocatalytic applications, as numerous enzymes undergo denaturation and subsequent deactivation at low pH. However, the CO_2 -induced decrease in pH can be exploited as an advantage in certain scenarios. Carbonic acid itself can function as a sustainable and cost-effective acidic reagent. Furthermore, the low pH of CO_2 –water mixtures proves beneficial for processes like H_2O_2 stability and decaffeination.

CO_2 exhibits a surprising level of solubility in H_2O , especially at low temperatures. This phenomenon can be attributed to strong solute–solvent interactions. Molecular dynamics studies by Sato et al. [134] provide compelling evidence for these interactions. Their work identified the formation of hydrogen bonds between an oxygen atom in CO_2 and a hydrogen atom in H_2O . This observation underscores the significance of site-specific interactions between CO_2 and H_2O molecules, surpassing the influence of dipole–quadrupole and dispersion interactions between water and CO_2 molecules. The study by Bowman et al. [135] suggests that the dipole–quadrupole interaction between water and CO_2 hinders the free rotation of the water molecule within the CO_2 environment. This could be due to the water molecule experiencing a stronger attraction in certain orientations relative to the CO_2 . The solubility isotherms of CO_2 in water are depicted in Figure 18.

The influence of electrostatic interactions on solvation has been studied in previous research [119,136]. The comparable charge separation between CO_2 and H_2O suggests the potential for significant site-specific interactions between solute molecules and CO_2 , akin to the observed enhanced CO_2 dissolution in water. However, the extensive network of cooperative hydrogen bonds in H_2O sets it apart as a unique solvent for polar materials. Despite this, the studies indicate that CO_2 can be considered a polar molecule due to the presence of two active and relatively strong bond dipoles. The vector sum of these dipoles cancels out, resulting in a zero net dipole moment but non-zero quadrupole moment. Solute– CO_2 interactions mediated by dipole–quadrupole forces are believed to be instrumental in imparting many of CO_2 's polar characteristics. Kauffman [137], for instance, showed that this type of interaction is responsible for the observed localized increase in density under near-critical conditions. Their study underscores the role of CO_2 's significant quadrupole moment in its solvation behaviour. The electronic structure of CO_2 , featuring partial negative charges on the electronegative oxygen atoms and a substantial partial positive charge on the central carbon atom, suggests its ability to function as both a weak Lewis acid and a Lewis base. Danten et al. [138] also suggested Lewis acid–base interactions in a water– CO_2 system in which CO_2 acts as a Lewis acid due to the central carbon having an empty orbital that can accept electrons. The lone electron pairs on the oxygen atom of water make it a Lewis base, a potential donor. The Lewis acid–base interaction can create a weak bond between the oxygen of water and the carbon of CO_2 . This additional attractive force, along with the dipole–quadrupole interaction, could further restrict the rotational freedom of water molecules in CO_2 compared to free water. Moreover, both these interactions are weaker compared to strong covalent bonds, which involve the sharing of electrons between atoms. This means that they can be disrupted or influenced more easily by factors like temperature and density. The extent of the Lewis acid–base interaction specifically might be further limited by the factors mentioned like solvent density and temperature. At lower CO_2 densities, there are fewer CO_2 molecules available for the oxygen atom of water to interact with, reducing the chances of Lewis acid–base bonding. Similarly, higher temperatures can increase the thermal motion of both water and CO_2 , making it harder for them to form and maintain this weak bond.

Tassaing et al. [139] used powerful tools such as infrared and vibrational spectroscopy to investigate water– CO_2 interactions in SC- CO_2 . Authors suggests the presence of local density inhomogeneities within SC- CO_2 . This means that the density of CO_2 molecules

might not be uniformly distributed around the water molecules. The observed red shift even at temperatures above the critical temperature ($T_r \geq 1.2$) indicates that attractive forces between water and CO_2 persist. The authors propose that these attractive forces lead to the clustering of CO_2 molecules around water molecules. This clustering creates areas with higher CO_2 density around water. Tabasinejad et al. [140] highlight the importance of considering molecular interactions (association) for accurate modelling, especially for the CO_2 -water system. By incorporating this association scheme (4C) into the aCPA-PR model, researchers could accurately predict CO_2 solubility across a wide range of pressures and temperatures.

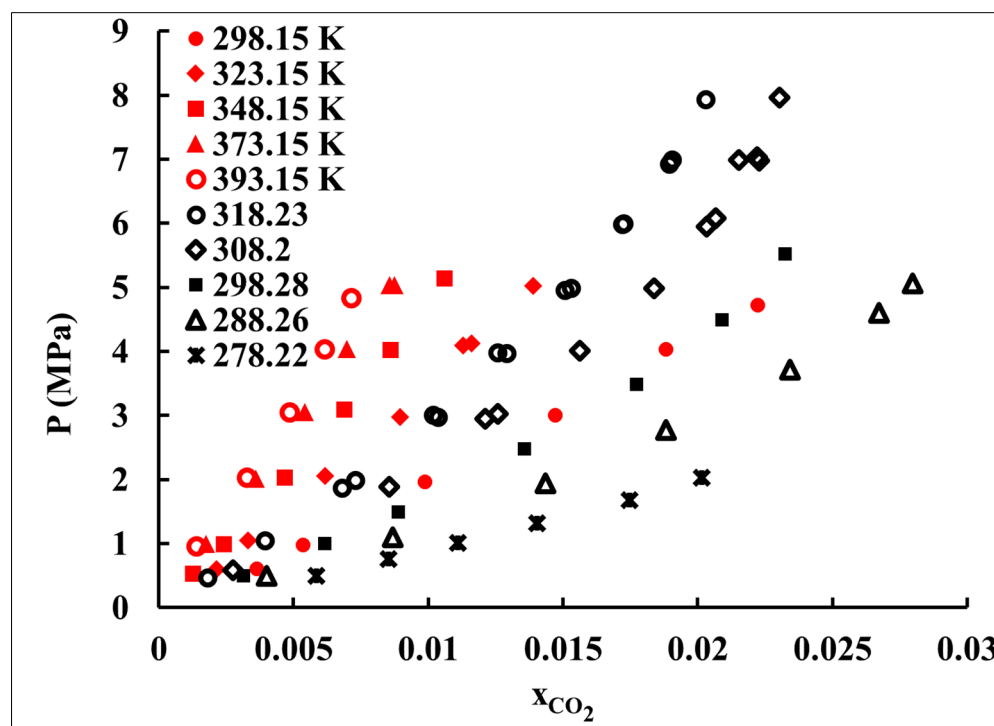


Figure 18. Solubility of CO_2 in water at various temperatures and pressures. Red symbols correspond to Ref. [141] and black symbols correspond to Ref. [142] for experimental data.

4.2.6. Monomer/ CO_2 and Polymer/ CO_2 /Cosolvent Mixtures

The potential of SCF solvents to revolutionize polymer processing has led to a surge in research and development in areas such as polymerization processes, polymer purification and fractionation, and environmentally friendly solutions. SCFs' lower density compared to liquids offers more free volume to the polymer chains. This increased free volume translates to enhanced chain mobility and diffusion, ultimately improving the polymer transport properties. However, to fully unlock this potential, a deeper understanding of the fundamental physics and chemistry behind how SCF solvents interact with polymers is crucial. This knowledge is the key to effectively utilizing SCF-based polymer processing technologies. The quality of the solvent, quantified by the interaction strength between the polymer segments and solvent molecules, plays a crucial role. "Good" solvents, which interact favourably with the polymer, lead to the formation of a homogeneous, single-phase solution. In contrast, "poor" solvents, which have unfavourable interactions, promote phase separation, resulting in distinct polymer- and solvent-rich phases. Understanding these factors is essential for predicting and controlling the phase behaviour of polymer solutions, which is critical for various applications in polymer science and engineering.

In this section we discuss the phase behaviour of monomers (Figure 19) and polymers (Figures 20 and 21) in CO₂.

The selection of CO₂ as a solvent for polymers necessitates careful consideration of the interplay between intermolecular forces and free volume effects. Solubility in this system is governed by the interplay between: (a) *Intermolecular interactions*: solvent–solvent, solvent–polymer segment, polymer segment–segment interactions. (b) *Free volume difference*: The disparity in free volume between the polymer and CO₂ is crucial. If the polymer is densely packed with minimal free volume, CO₂ molecules may struggle to penetrate and achieve effective solvation. (c) *CO₂'s selectivity*: These CO₂–polymer interactions can be inherently weaker compared to the cohesive forces holding nonpolar polymer chains together. Consequently, CO₂ may have limited effectiveness in disrupting these cohesive forces and dissolving nonpolar polymers. For highly polar polymers, dipole–dipole interactions between polymer segments become more prominent, especially at low temperatures. These strong interactions can hinder CO₂ molecules from approaching and effectively solvating the polymer.

The dissolution of a polymer in CO₂ is therefore governed by a complex interplay between intermolecular forces and the free volume available within the system. Favourable interactions between CO₂ and individual polymer segments, quantified by the interchange energy, are crucial for overcoming the polymer–polymer interactions and the self-association tendency of CO₂ molecules. Additionally, the free volume difference between the densely packed polymer chains and the relatively small CO₂ molecules dictates the accessibility of the polymer for CO₂ solvation. These factors collectively determine the pressure and temperature conditions required to achieve sufficient CO₂ uptake by the polymer. Due to its structural symmetry, CO₂ lacks a permanent dipole moment and relies on quadrupole interactions, which operate at shorter distances compared to dipole–dipole interactions. As a solvent for polymers, CO₂ exhibits selectivity. At lower temperatures, the dominance of CO₂–CO₂ quadrupole interactions makes it a weak solvent for nonpolar polymers, as the interchange energy favours CO₂ self-association. Conversely, highly polar polymers present a challenge due to strong dipole–dipole interactions that outweigh CO₂ quadrupolar forces, especially at lower temperatures, where these interactions are further enhanced [143]. Solubility data for monomer units and polymers in CO₂ are presented in the Supplementary Materials (Table S9).

Several authors have performed spectroscopic studies to analyze molecular interactions in CO₂–polymer systems [144,145]. Traditionally, CO₂ solubility in polymers was believed to be solely dependent on pressure and temperature. However, recent research has revealed a more nuanced picture. Even under identical pressure and temperature conditions, the amount of CO₂ dissolved varies significantly between different polymers. This variation can be attributed to the specific intermolecular interactions occurring between CO₂ and the polymer. Notably, Lewis acid–base interactions are a prevalent type of interaction observed in these systems. The evidence of weak Lewis acid–base interactions between polymers and CO₂ has been confirmed by Nalawade et al. [146] using FT-IR spectroscopic studies. Quantitative analysis of the FT-IR spectra revealed a greater interaction strength between CO₂ and the polymers containing ether groups compared to those with ester groups. Kazarian and colleagues' findings [128] revealed that polymers containing electron-donating groups, specifically those with carbonyl functionalities (C=O), exhibit specific interactions with CO₂. This attraction arises due to an electron donor–acceptor interaction. The carbonyl oxygen in the polymer donates electron density towards the electron-deficient carbon atom in CO₂. However, these interactions are relatively weak, typically less than 1 kcal/mol, which is only slightly stronger than dispersion forces. While Kazarian et al. [128] identified this specific interaction, its weak nature suggests that addi-

tional factors, such as high pressure or low temperature, might be necessary for substantial CO₂ uptake by certain polymers.

High molecular weight polymers and those with broad molecular weight distributions exhibit reduced solubility due to increased chain entanglement, fewer available chain ends, and excluded volumes. Additionally, the degree and type of chain branching significantly impact solubility. Branching, particularly with short side chains, can disrupt efficient chain packing and promote solubility compared to linear polymers. However, long-chain branches can behave similarly to linear chains, diminishing their positive impact on solubility. Flexible polymer chains tend to dissolve CO₂ more easily, leading to a lower cloud point pressure [147].

The placement of CO₂-philic groups within a polymer's structure critically influences its solubility in CO₂. Polymers with CO₂-philic moieties located in accessible side chains exhibit a significantly higher affinity for CO₂ compared to those with moieties embedded within the denser main chain. This difference arises from inherent packing constraints. The polymer's main chain, serving as the structural backbone, typically has a denser configuration with stronger intermolecular interactions, which can lead to steric hindrance that limits effective contact between CO₂ molecules and CO₂-philic groups within the main chain. In contrast, side chains provide a more open and accessible environment, facilitating greater interaction between CO₂ molecules and CO₂-philic moieties, ultimately enhancing CO₂ solubility [148]. Hyperbranched and star polymers provide significant advantages over linear polymers due to their enhanced free volume and reduced chain entanglement. These features facilitate easier dissolution (solubilization) at lower pressures, potentially leading to more efficient processing in various applications. [148,149].

Due to the inherent polydispersity of polymers, the transition between single-phase and two-phase regions in a polymer–fluid mixture lacks a sharp boundary. Consequently, the cloud point refers to the range of conditions (pressure, temperature, and concentration) where this gradual transition occurs, reflecting the varying response of different chain lengths to changes in miscibility. By analyzing cloud point behaviour, researchers gain insights into intermolecular interactions between polymer segments and fluid molecules, including both segment–segment interactions and segment–fluid interactions. Notably, the cloud point is sensitive to both the molecular weight of the polymer chains and the specific interactions between segments and the fluid [147]. Polar groups accessible in the polymer backbone or side chains can specifically interact with CO₂ through dipole–quadrupole interactions. This specific interaction is generally stronger than interactions between CO₂ and non-polar groups. As a result, the solubility of CO₂ in polymers increases with the increasing content of polar groups in the polymer, further lowering the cloud point pressure.

DeFelice's work [150] offers valuable insights into the relationship between polymer structure and CO₂ miscibility. The study compares the properties of various polymer–CO₂ mixtures with the pure components' characteristics, specifically focusing on free volume and interaction energy. Their analysis reveals a clear trend: polymers with high free volume and weak segment–segment interaction energies exhibit a greater propensity to mix favourably with CO₂. This suggests that a key factor governing CO₂ solubility in polymers is the availability of space within the polymer structure to accommodate CO₂ molecules. Additionally, weaker interactions between polymer segments allow for less resistance to the incorporation of CO₂, facilitating more favourable mixing.

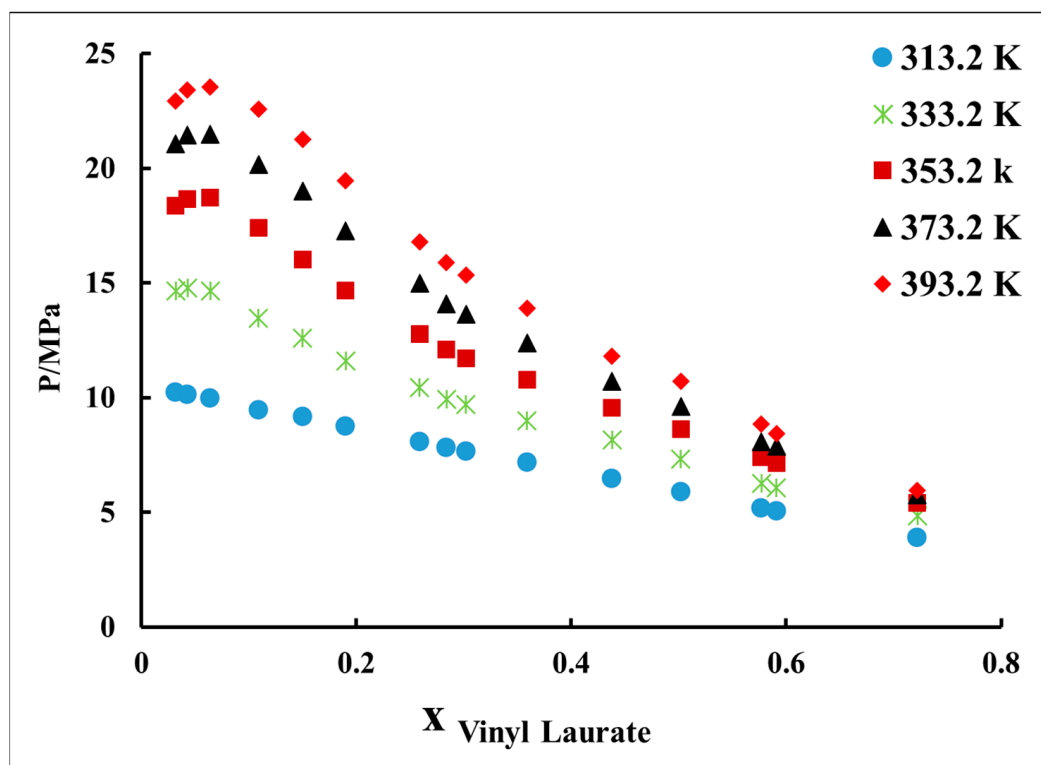


Figure 19. Solubility of vinyl methacrylate in CO₂ at various temperatures. Experimental data is taken from [151].

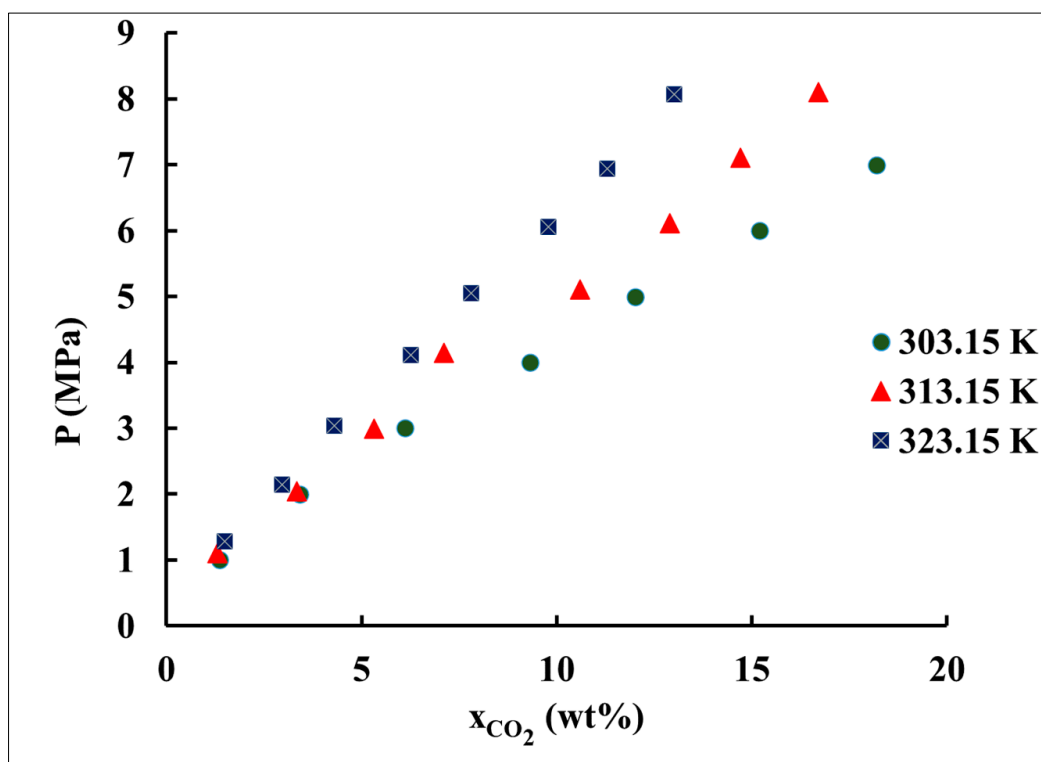


Figure 20. Solubility of CO₂ in poly(ethylene glycol) 200 at several temperatures. Experimental data are taken from [152].

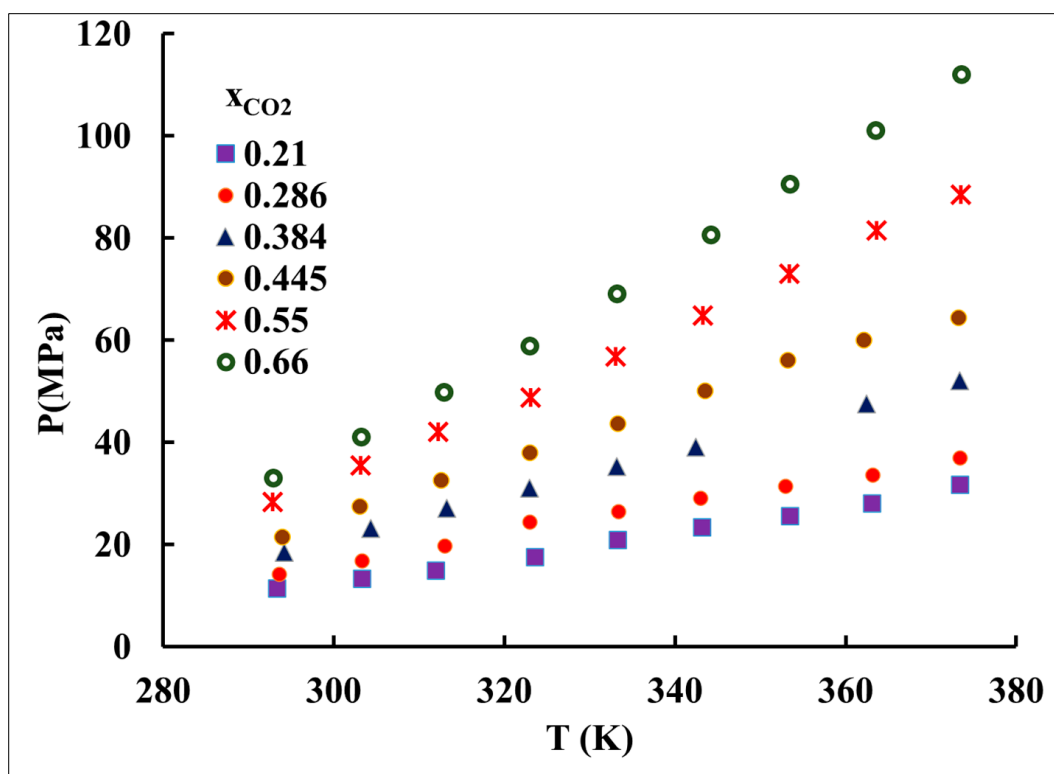


Figure 21. Pressure vs. temperature plot for poly(ethylene glycol) dimethyl ether in CO₂. Experimental data is taken from [153].

4.2.7. Ionic Liquid/CO₂ Binary Systems

The study of binary systems involving ionic liquids (ILs) and CO₂ has garnered significant interest due to the unique properties and potential applications of these mixtures. ILs, characterized by their low volatility, negligible vapour pressure, an extensive liquid range, high thermal stability, and tunable solvation properties, when combined with CO₂, particularly in its near-critical and supercritical states, offer promising avenues in green chemistry, material science, and separation technologies. ILs are molten salts predominantly consisting of large, asymmetric organic cations paired with smaller inorganic or organic anions. These substances exhibit low melting points, often below 100 °C and frequently below ambient temperature. Furthermore, the physicochemical properties of ILs can be extensively tuned by altering or modifying their anionic and cationic components to optimize CO₂ absorption and other critical attributes [154]. SC-CO₂ is highly soluble in ILs, while the solubility of IL in SC-CO₂ is low. SC-CO₂ can create distinct two-phase systems when combined with non-volatile and polar ILs. Such ILs/SC-CO₂ systems remain biphasic even at high pressure up to 40 MPa [155]. The recovery process in these systems relies on the fact that SC-CO₂ dissolves in ILs, whereas ILs do not dissolve in SC-CO₂ [156]. Because most organic compounds dissolve readily in SC-CO₂, they can be efficiently transferred from the IL phase to the SC-CO₂ phase due to the high solubility of SC-CO₂ in ILs [157]. The present discussion will focus on the phase behaviour, molecular interactions, and thermodynamic properties of binary mixtures of ILs and CO₂. Although most research concentrates on the solubility of CO₂ in ILs, it is equally important to investigate the concentration of ILs in the CO₂-rich phase. The low solubility of ILs in CO₂ has been attributed to the following reasons: ILs have extremely low vapour pressure and CO₂ cannot adequately solvate ions in its gaseous phase. Studies have shown that while the solubility of ILs in SC-CO₂ is generally very low and often negligible, the presence of other components, such as reactants and products, can significantly influence this solubility [158,159]. The unique properties

of IL-CO₂ mixtures can also be exploited in the synthesis of advanced materials, such as nanoparticles and porous materials, where phase behaviour and solvation properties play a critical role. Furthermore, ILs and SC-CO₂ have been used to improve the efficiency and selectivity of the EOR process [160,161].

The solubility of CO₂ in ILs generally increases with pressure and decreases with temperature, as illustrated in Figure 22. Figure 22 illustrates experimental vapour–liquid equilibrium data for [EMIm][Tf₂N] and CO₂ at 298.15 K, 323.15 K, and 343.15 K. At a given temperature, the solubility of CO₂ in ILs initially increases with rising pressure. However, at very high pressures, the solubility plateaus because the available free volume within the IL becomes fully occupied by CO₂ molecules. Consequently, adding more CO₂ molecules is nearly impossible unless the strong cohesive structure of the IL is disrupted. Studies indicate that anion–CO₂ interactions significantly influence CO₂ solubility in ILs. Kazarian et al. and Cadena et al. showed through ATR-IR spectroscopy and combined experimental and computational methods that these interactions can be characterized by CO₂ acting as a Lewis acid and anions as Lewis bases [162,163]. Modifying the cation structure also impacts CO₂ solubility, though to a lesser extent than anion identity, as illustrated in Figure 23. The effect of cation alkyl-group length on CO₂ solubility was compared for ILs with the same anion [Tf₂N] [164] (Figure 23). Increasing the alkyl length from [EMIm] to [HMIm] to [DMIm] results in only a slight increase in CO₂ solubility. This suggests that the anion has a greater impact on solubility than the cation's alkyl length. The alkyl group enhances the cation's dispersion forces for better interaction with CO₂. For instance, substituting the acidic proton at the C2 position of the imidazolium ring with groups such as methyl, ether, hydroxyl, nitrile, or alkyne reduces CO₂ solubility [165]. Increasing the alkyl chain length on the cations enhances CO₂ solubility, although this effect is secondary to anion influence [166]. The presence of preformed cavities in ILs and the availability of free volume are critical factors in determining CO₂ solubility. Studies using MD simulations and Voronoi algorithms have shown that CO₂ solubility is influenced by the ability of IL structures to accommodate CO₂ molecules through cavity formation, which is facilitated by weak cation–anion interactions [167]. According to Huang et al., when SC-CO₂ dissolves in an ionic liquid, it exhibits a much smaller partial molar volume than when it is dissolved in most other solvents [167]. As mentioned by Keskin et al., the effect of a high degree of CO₂ solubility on the viscosity of ILs is significant [157]. Dissolution of CO₂ in ILs leads to a reduction in viscosity, which can be quantitatively assessed by measuring the decrease in drag on the stirring magnet within a static high-pressure vapour–liquid equilibrium setup. This reduction in viscosity enhances the efficiency of the solution process.

The miscibility of ILs with CO₂ can vary significantly; some ILs are completely miscible with SC-CO₂, while others exhibit limited miscibility, leading to the formation of distinct phases. Experimental methods such as gravimetric methods, isochoric saturation methods, synthetic (bubble point) methods, etc., are used to measure the solubility of gases in ILs [165]. Over the past decade, a substantial amount of data on CO₂ solubility in ILs has been published, summarizing experimental solubility data, including CO₂ mole fraction, temperature, pressure, and type of data. Huang et al. [167] described an intriguing phenomenon in solutions of CO₂ and ionic liquids, where the partial molar volume of CO₂ is significantly smaller in the IL phase compared to bulk SC-CO₂ under identical temperature and pressure conditions. Remarkably, the partial molar volume of CO₂ in the IL phase is so low that the dissolved CO₂ molecules occupy a space nearly equivalent to their van der Waals volume. This indicates the strong electrostatic interactions between the CO₂ molecules and the ILS. In certain IL-CO₂ systems, phase separation occurs due to differences in polarity and molecular size. The presence of CO₂ can induce phase transitions in ILs, such as liquid–liquid demixing or the formation of a supercritical fluid phase.

The dissolution of CO₂ in ILs can occur through either physical or chemical absorption mechanisms. Physical absorption of CO₂ in ILs is most effective under conditions of high pressure and low temperature [165]. The captured CO₂ can be easily released, and the ILs regenerated, by subsequently reducing the pressure and increasing the temperature. In contrast, chemical absorption may involve a reaction between CO₂ and the IL medium [168]. ILs suitable for chemical absorption often contain functional groups such as amines, acetate, and cyanates, achieving higher CO₂ solubility compared to those relying on physical absorption alone. However, due to their high viscosity and significant energy requirements for CO₂ desorption, they are less feasible for industrial-scale applications. Imidazolium-based ionic liquids have been the primary focus of CO₂ solubility studies due to their widespread availability and demonstrated capacity for CO₂ absorption. ILs are favoured among various adsorption-based materials because of their high thermal stability, non-corrosiveness, nonvolatility, nonflammability, and high selectivity for CO₂ adsorption at both high temperatures and room temperature [169,170]. Additionally, the solubility and adsorption capacity of CO₂ in ILs are influenced by the nature of their anionic groups. ILs with fluorinated alkyl groups exhibit superior solubility, whereas those with acetate anions demonstrate better adsorption capacity [171,172].

The molecular interactions between ILs and CO₂ are critical in determining the phase behaviour and properties of the mixture. The interaction strengths between CO₂ and ions in ILs are influenced by the hydrophilicity, or polarity, of the ions. Hydrophilic ions tend to have stronger interactions with CO₂ [154]. Keskin et al. revealed several key insights into molecular interactions between ILs and CO₂ [157]: (1) *Lewis Acid–Base Complex Formation*: In situ attenuated total reflectance-infrared (ATR-IR) spectroscopy has shown that CO₂ forms weak Lewis acid–base complexes with the anions in ILs. The size and strength of the anion impact the interaction, with larger anions exhibiting weaker interactions. (2) *Solubility Influences*: There are factors beyond the strength of the Lewis acid–base interaction that influence CO₂ solubility. Specifically, the free volume within the IL, affected by the strength of anion–cation interactions, plays a significant role. Weaker anion–cation interactions in ILs lead to more available free volume, facilitating greater CO₂ solubility. (3) *Effect on Melting Points*: ILs are characterized by their low melting points, and high-pressure CO₂ can further reduce these melting temperatures. This reduction is attributed to the weak Lewis acid–base interaction between the anion and CO₂, which disrupts the stronger interactions between anions and cations. The presence of CO₂ disrupts cation–anion and tail–tail interactions, thereby lowering the melting point of the IL. (4) *Application Potential*: The ability of high-pressure CO₂ to lower the melting points of ILs opens new possibilities for using ILs as solvents at milder temperatures. This effect has been observed in several analogous ILs, suggesting broader applicability in various industrial processes where lower operational temperatures are advantageous.

The unique phase behaviour and molecular interactions in IL–CO₂ systems open up numerous applications. CO₂ capture from industrial emissions is effectively achieved using ILs with high CO₂ solubility. The polar nature of ILs, which arises from the asymmetry of their ions, enhances their ability to capture CO₂. Furthermore, the captured CO₂ in ILs can be converted into useful chemicals, such as methanoic acid (HCOOH) [173,174]. The tunability of IL properties allows for the design of efficient capture processes [175]. In reviewing the role of ionic liquids in CO₂ capture, several prevalent myths have been dispelled by Carvalho et al. [176]: (1) *Myth of High Solubility*: A common misconception is that conventional ionic liquids exhibit exceptionally high CO₂ solubility. However, it has been demonstrated that their apparent high solubility is primarily a result of their high molecular weight, rather than an intrinsic ability to dissolve CO₂. (2) *Effectiveness of Conventional Enhancement Methods*: It was widely believed that standard approaches to

increase CO₂ solubility in ionic liquids were effective. This review reveals that, with the notable exception of the [B(CN)₄] anion, these conventional enhancement methods do not significantly improve CO₂ solubility. (3) *Universal Efficacy in CO₂ Capture*: There is a misconception that ionic liquids are effective for CO₂ capture across all applications. This review clarifies that while ionic liquids have shown success in chemical sorption of CO₂, they are not particularly effective as physical sorbents for CO₂.

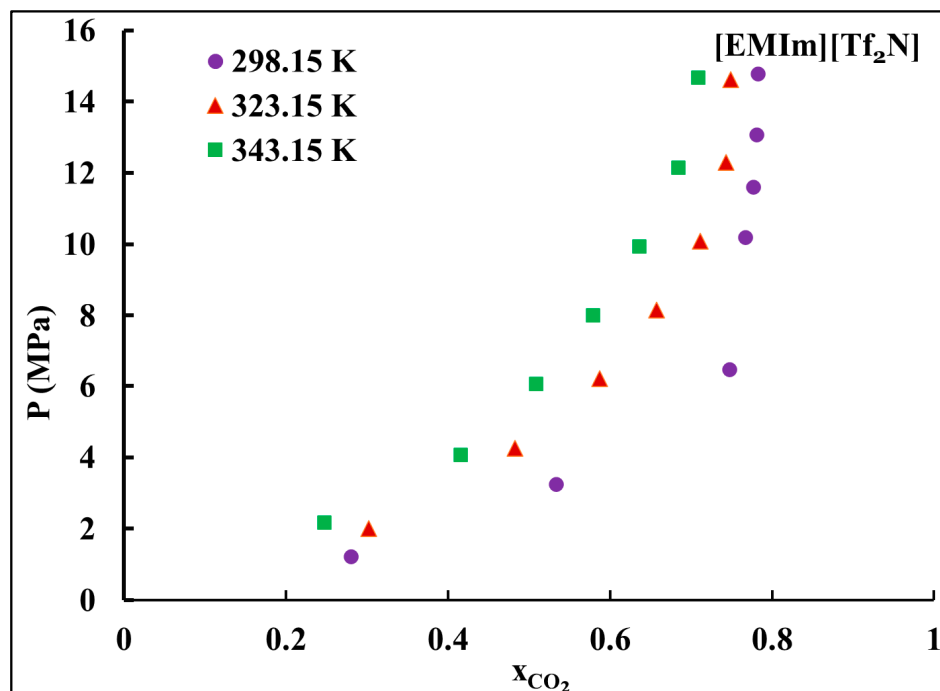


Figure 22. Experimental vapour–liquid equilibrium data for [EMIm][Tf₂N] and CO₂ at several temperatures [164].

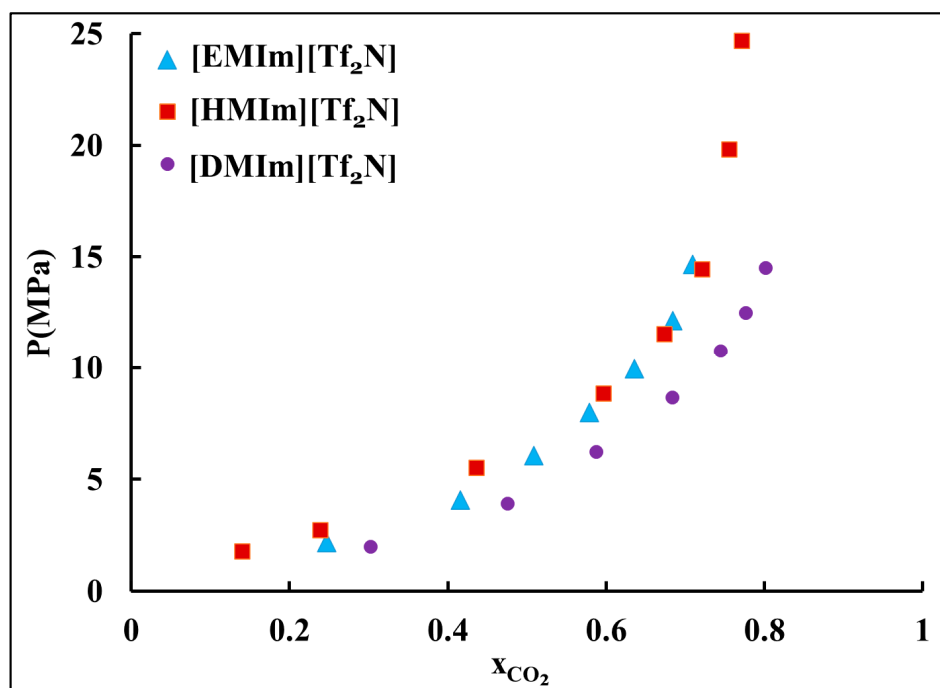


Figure 23. Experimental vapour–liquid equilibrium data for ILs and CO₂ at 343.15 K [164].

The phase behaviour of IL–SC–CO₂ systems, especially involving [bmim][PF₆] and CO₂, have been extensively studied to understand their high-pressure VLE [163]. Blanchard et al. used both static and dynamic apparatus to measure the solubility of CO₂ in [bmim][PF₆], noting that CO₂ solubility increases with pressure and decreases with temperature, albeit the temperature effect being minimal within the studied range [156]. The solubility data vary among studies, likely due to differing water content in the IL samples; dried samples show decreased CO₂ solubility compared to those with higher water content. This variability underscores the importance of IL sample preparation in phase behaviour studies. Researchers have demonstrated that SC–CO₂ can effectively extract non-volatile organic compounds from ILs with minimal contamination [155]. Furthermore, researchers also explored the use of supercritical CO₂ to separate ILs from their organic solvents. The introduction of SC–CO₂ causes the formation of an additional liquid phase that is rich in IL, even if the initial solution has a low concentration of IL [177]. Key findings indicate that CO₂ is highly soluble in ILs like [bmim][PF₆] and can be used to extract compounds such as naphthalene with high recovery rates. The process is reversible, leaving pure ILs after extraction and depressurization [178]. SC–CO₂ shows a strong ability to separate organic solutes based on their polarity, with nonpolar solutes being more easily extracted. This method presents a significant advantage for recovering high-boiling point and thermally sensitive compounds, highlighting the potential of SC–CO₂ in green chemistry applications for IL-based systems [155].

The study of binary mixtures of ionic liquids and CO₂, particularly in near-critical and supercritical states, reveals complex and tunable phase behaviour driven by intricate molecular interactions. The thermodynamic properties and phase diagrams of these systems are critical for designing efficient processes in various industrial applications, from CO₂ capture to green chemistry. Future research should focus on expanding the database of IL–CO₂ systems, exploring new ILs with tailored properties, and optimizing the conditions for specific applications. Understanding the fundamental interactions at the molecular level will further enhance the practical utility of these fascinating binary systems.

4.2.8. Deep Eutectic Solvent/CO₂ Mixtures

Deep eutectic solvents (DESs) are formed by combining Lewis or Brønsted acids and bases, specifically hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs), which together create an eutectic mixture [179]. The individual components of DESs interact through an intricate hydrogen bonding network, leading to a marked decrease in freezing point relative to the pure substances [180]. DESs exhibit many characteristics akin to ionic liquids, including low vapour pressure, toxicity, a broad liquid state range, high thermal stability, tunability, and non-flammability [181]. However, unlike ionic liquids, which are composed solely of discrete ions, DESs are mixtures of different compounds. One significant advantage of DESs over ionic liquids is their production from readily available and renewable resources, such as ammonium salts, sugars, amino acids, and organic acids, through simple mixing processes. This makes DESs not only more cost-effective but also potentially biodegradable [179]. By adjusting the components and their molar ratios, DESs can be tailored to achieve specific properties, such as enhanced CO₂ absorption capacity [182]. Managing CO₂ emissions is crucial for sustainable technology development, especially given the 40% increase in greenhouse gas emissions since the “World Scientists’ Warning to Humanity” manifesto in 2022. Conventional amine-based absorbents face issues like corrosion and high energy costs, highlighting the need for new, environmentally friendly CO₂ capture solutions [179]. ILs have been the focus of extensive research for their potential in CO₂ capture [183]. Nonetheless, their high cost, stemming from intricate synthesis and purification methods, limits their practicality. Consequently, DESs have gained

attention as cost-effective and promising alternatives for CO₂ capture. Makarov et al. [179] demonstrated the potential of DESs as CO₂ absorbents by predicting CO₂ solubility in DESs via proposed models. The study employs machine learning models to screen potential DESs for CO₂ absorption. By developing models to predict CO₂ solubility and melting temperatures in hydrogen bond acceptor/donor systems and using a diverse dataset of DESs and ionic liquids, the researchers identified 1447 mixtures with high CO₂ absorption capacity. However, only five DESs were recommended for further consideration due to their lack of chemical reactivity with CO₂.

Sarmad et al. [184] evaluated DESs based on their viscosity and CO₂ solubility, which are essential parameters for the effective design of CO₂ absorbents. Viscosity, a measure of a fluid resistance to flow and internal friction, is notably higher in DESs compared to other organic solvents, similar to conventional ionic liquids. This elevated viscosity poses challenges in handling, filtering, and stirring, making it a critical parameter for industrial applications like CO₂ capture. During CO₂ capture, some DESs experience an increase in viscosity as the amount of CO₂ absorbed rises, leading to reduced heat and mass transfer rates, decreased CO₂ absorption efficiency, and higher energy consumption. Thus, achieving a balance between viscosity and CO₂ absorption capacity is essential for efficient CO₂ capture. Viscosity in DESs is impacted by various factors: increasing temperature decreases it, the presence and type of HBD can significantly raise it due to hydrogen bond formation, longer alkyl chains in HBD increase viscosity, higher molar ratios of HBD to salt decrease viscosity, and the inclusion of a co-HBD can substantially reduce viscosity. Understanding these influences is crucial for optimizing DESs for applications such as CO₂ capture.

Figure 24 illustrates the bubble points for the lactic acid chloride system (2:1 molar ratio) with varying CO₂ molar fractions across different temperatures, providing valuable insights into CO₂ solubility in this DES. As the temperature increases, the bubble point pressures rise for all CO₂ concentrations, indicating a decrease in solubility at higher temperatures due to the need for higher pressures to maintain CO₂ in the dissolved state. Higher CO₂ molar fractions correspond to higher bubble point pressures, demonstrating a consistent linear relationship between temperature and pressure, which suggests stable thermodynamic behaviour of the DES across the temperature range. This trend highlights the potential of the lactic acid chloride mixture for CO₂ capture and storage applications, where adjusting temperature and CO₂ concentration can optimize performance. The predictable solubility patterns underscore the unique interactions within this DES system, making it a promising candidate for industrial processes requiring CO₂ absorption. Similarly, several solubility isotherms, measured at temperatures of 303.15 K, 313.15 K, 323.15 K, and 333.15 K, are presented in Figure 25, for the pseudo-binary system of CO₂ with a DES composed of 1 mole of choline chloride (ChCl) and 3 moles of triethylene glycol. The experiments reveal that CO₂ solubility increases with pressure at a constant temperature, confirming the system's capacity to absorb more CO₂ as pressure rises. Additionally, the data shows that lower temperatures result in higher CO₂ solubility at a given pressure, reflecting the inverse relationship between temperature and gas solubility. The isotherms are linear across the pressure range studied, with no intersections, indicating consistent behaviour across the temperature spectrum. The validation of the lower pressure data against the existing literature further supports the reliability and accuracy of the high-pressure solubility data presented. The absence of intersections among the isotherms confirms that each temperature follows a distinct solubility path, emphasizing the temperature-dependent nature of CO₂ solubility in this DES system. These findings underscore the practical relevance of this DES in CO₂ capture and storage applications, where temperature and pressure can be controlled to optimize CO₂ absorption. The consistent and predictable solubility

behaviour across different temperatures makes this DES system a promising candidate for such applications, contributing to a broader understanding of CO₂ solubility in DESs and offering valuable insights for future research and industrial use.

Over time, numerous experimental techniques have been devised to quantify CO₂ solubility in DESs [185]. Among the most widely used are the isochoric saturation and gravimetric methods. Less commonly employed methods include the pressure drop technique and the magnetic suspension balance approach. These techniques facilitate measurements across diverse temperatures and pressures, typically assuming that DESs have negligible vapour pressure. The HBA significantly impacts the CO₂ absorption capacity of DESs [185]. Research indicates that DESs with larger cations, such as those based on Tetrabutylammonium Chloride and Tetrabutylammonium Bromide, exhibit higher CO₂ solubility compared to those with smaller cations like Tetraethylammonium Chloride and Tetraethylammonium Bromide, due to the greater free volume of the sorbent [166,186]. The effect of the anion is modest, with slight increases in solubility when chloride is replaced by bromide [187]. Additionally, the symmetry and chemical nature of the HBA influence CO₂ solubility; for instance, DESs with ester groups or COO[−] groups have better CO₂ affinity compared to those with hydroxyl or COOH groups [188]. The nature of the HBD in DESs significantly affects CO₂ absorption. Amines and alkanolamines as HBDs lead to chemical absorption through reactions with CO₂, whereas other HBDs like amides, glycols, sugars, and acids result in physical absorption [185]. Factors influencing CO₂ solubility include the positioning of hydroxyl groups, alkyl chain length, ether groups, and the functional group chemistry of the HBD. Generally, DESs with larger free volumes, specific functional groups, and lower steric hindrance exhibit higher CO₂ solubility, with amides, carbonyl groups, and ether bonds providing stronger interactions compared to hydroxyl groups [189]. Additionally, alkanolamines and amines tend to enhance CO₂ solubility through chemical interactions, particularly when featuring longer alkyl chains and more amine groups [190]. The molar ratio of HBA to HBD significantly influences CO₂ solubility in DESs. For some DESs, such as ChCl:2,3-butanediol, increasing the HBD amount enhances CO₂ solubility, while for others like ChCl:1,4-butanediol, it decreases [191]. The solubility in DESs based on allyltriphenylphosphonium bromide decreases with more HBD due to reduced molar and free volume, but DESs like ChCl show increased solubility with higher HBD ratios, likely due to weaker hydrogen bonds [187,192,193]. Lower viscosity and increased fluidity at higher HBA/HBD ratios also improve CO₂ absorption, as seen in DESs based on various amines and alkanolamines. However, some DESs exhibit decreased solubility at higher ratios, highlighting the complex and unpredictable nature of these systems [194]. The synergistic effect between HBDs and HBAs in DESs significantly impacts CO₂ absorption capacity. Researchers like Shukla and Mikkola explored solvatochromic polarity parameters, which include electronic transition energy (ET(30)), dipolarity/polarizability (π^*), hydrogen bond donor acidity (α), and hydrogen bond acceptor basicity (β), to understand intermolecular interactions in DESs [195]. They found that a balanced equilibrium between α and β , where $|\alpha - \beta|$ is close to zero, enhances CO₂ solubility. This synergistic effect occurs when the standard enthalpy and entropy changes are positive, and ET(30) is low, suggesting stable sites for CO₂ interaction. However, this relationship is complex and can be influenced by other factors such as free volume and the strength of hydrogen bonds within the DES.

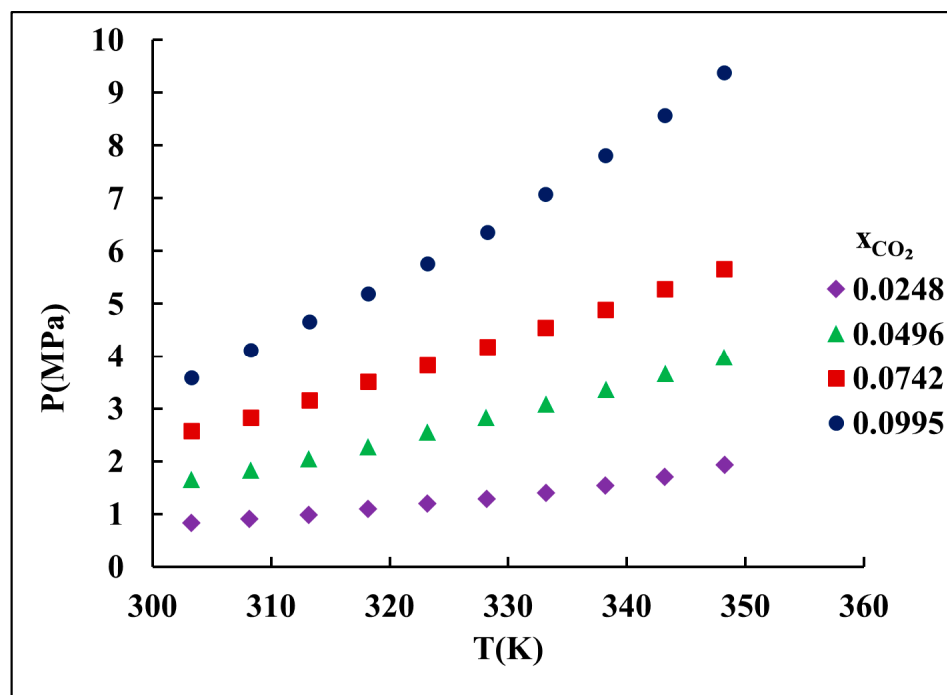


Figure 24. Bubble points of lactic acid/chloride mixture with a 2:1 molar ratio + CO₂ at varying molar fractions of CO₂ [196]. The symbols indicate experimental data for isopleths corresponding to different CO₂ concentrations.

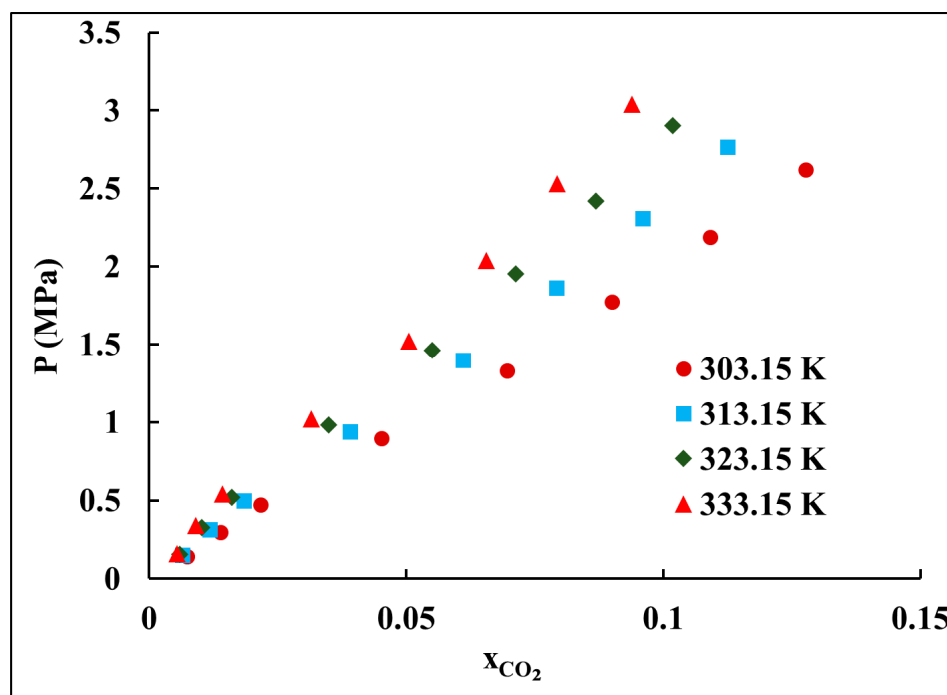


Figure 25. Solubility isotherms for the pseudo-binary systems of CO₂ + DES (1 ChCl +3 triethylene glycol) [197].

4.3. Data Consistency Assessment

To enhance the reliability and interpretability of the compiled experimental phase-equilibrium data, consistency among literature sources was qualitatively assessed. This consideration is particularly important for CO₂-containing and SCF systems, where reported data may exhibit systematic discrepancies arising from differences in experimental methodologies (e.g., analytical versus synthetic approaches, sampling versus non-sampling

techniques), sample purity, equilibrium detection criteria, and calibration of pressure, temperature, and composition measurements. Such discrepancies may manifest as variations in reported solubilities (mole fraction, x), shifts in phase boundaries, or differences in critical parameters, which can influence thermodynamic modelling and process design.

In the Supplementary Materials, the term “reference-quality data” is used to denote experimental datasets that are particularly suitable for benchmarking thermodynamic models and supporting engineering applications. These datasets are identified based on qualitative reliability criteria, rather than quantitative re-analysis, including: (i) application of well-established high-pressure experimental methodologies, particularly non-sampling or in situ techniques that minimize depressurization artefacts; (ii) clear reporting of calibration procedures and uncertainty estimates for pressure, temperature, and composition; (iii) qualitative agreement or reproducibility with independent studies over comparable pressure–temperature ranges; and (iv) frequent use of the data in subsequent modelling, validation, or application-oriented studies.

Datasets satisfying multiple criteria are highlighted in the Supplementary Materials to guide readers toward literature sources that are generally regarded as reliable within the thermodynamics and supercritical fluids community.

5. Conclusions

5.1. Summary of Key Findings and Insights from the Review

This review provides a comprehensive overview of the complex phase behaviour exhibited by binary mixtures containing near-critical and SC-CO₂. A critical analysis of experimental methodologies, encompassing both analytical and synthetic approaches, has been conducted to elucidate the strengths and limitations of each technique in determining phase equilibria. A cornerstone of this review is the exploration of the effect of the intricate relationship between pressure, temperature, and the nature of components on phase behaviour. The influence of molecular interactions, including those within ionic liquids, deep eutectic solvents, and polymers, on phase equilibria has been meticulously examined. The concept of free volume and its impact on solubility and phase transitions has also been highlighted.

This review meticulously compiles experimental phase equilibrium data for a wide range of binary systems involving near-critical and supercritical CO₂, highlighting critical trends and behaviours across diverse solvent–solute pairs. The comprehensive data tables (Supplementary Materials), provide detailed insights into phase behavior under varying conditions of temperature, pressure, and composition. These findings emphasize the versatility and adaptability of SC-CO₂ as a solvent, showcasing its interactions with hydrocarbons, alcohols, ethers, and other solutes. By systematically documenting and analyzing these binary systems, the review offers a valuable resource for researchers, aiding in the validation of thermodynamic models and the development of industrial processes. Furthermore, the role of cosolvents in modulating phase behaviour has been addressed, emphasizing their potential to enhance solubility and alter phase boundaries. The review underscores the importance of understanding these fundamental principles for the successful design and optimization of processes involving SC-CO₂.

5.2. Implications of Understanding Phase Behaviour in Near-Critical and SC-CO₂ Systems

A profound comprehension of phase behaviour in near-critical and SC-CO₂ systems is instrumental in advancing various industrial sectors. By elucidating the factors governing phase equilibria, researchers and engineers can optimize processes such as extraction, separation, and purification. For instance, the ability to predict the solubility of solutes in SC-CO₂ enables the design of efficient extraction processes, minimizing solvent consumption

and energy expenditure. Furthermore, understanding phase behaviour is crucial for developing novel materials and formulations. By tailoring the properties of SC-CO₂ through the addition of cosolvents or the application of pressure and temperature, it is possible to create materials with specific properties and functionalities. The pharmaceutical industry, for example, can leverage this knowledge to develop controlled-release drug delivery systems and enhance drug solubility.

The extensive experimental data presented in this review underscore the importance of understanding phase behaviour for the efficient utilization of supercritical CO₂ in industrial applications. These insights are particularly critical for optimizing separation processes, solvent recycling, and material synthesis, where precise control over phase equilibria is essential. The availability of such detailed datasets not only enhances predictive modelling but also bridges the gap between experimental and theoretical frameworks. This deeper understanding of binary mixtures involving SC-CO₂ can drive innovation in areas such as green chemistry, pharmaceuticals, and sustainable energy solutions. Moreover, the exploration of phase behaviour in SC-CO₂ systems contributes to the development of sustainable and environmentally friendly technologies. By utilizing SC-CO₂ as a green solvent, it is possible to reduce the use of hazardous organic solvents and minimize waste generation. Additionally, the ability to tune the properties of SC-CO₂ offers opportunities for the recovery and recycling of valuable materials from waste streams.

5.3. Closing Remarks

The field of high-pressure phase equilibria involving SC-CO₂ is poised for significant advancements. Several promising avenues for future research can be envisioned: (1) *Advanced Experimental Techniques*: The development of in situ spectroscopic and scattering techniques will enable real-time monitoring of phase transitions and molecular interactions. (2) *Computational Modelling*: Improved computational models capable of accurately predicting phase behaviour over a wide range of conditions will be essential for process design and optimization. (3) *Novel Solvent Systems*: Exploring new solvent systems, such as ionic liquids and deep eutectic solvents, in combination with SC-CO₂ to enhance selectivity and efficiency. (4) *Green and Sustainable Processes*: Focusing on developing environmentally friendly processes utilizing SC-CO₂, such as waste treatment, recycling, and resource recovery. (5) *Multiphase Reactors*: Designing and optimizing multiphase reactors for efficient reactions and separations involving SC-CO₂. (6) *Process Intensification*: Combining SC-CO₂ technology with other process intensification techniques to improve energy efficiency and productivity.

Emerging technologies such as microfluidics and additive manufacturing are expected to play a crucial role in advancing SC-CO₂ phase behaviour studies. Integrating these technologies with advanced characterization techniques will enable the investigation of complex systems and the development of novel processes. In conclusion, a deep understanding of phase behaviour in SC-CO₂ systems is crucial for the development of sustainable and efficient technologies. By combining experimental and theoretical approaches, and by embracing emerging technologies, significant progress can be made in this field. The inclusion of extensive experimental phase equilibrium data in this review sets a benchmark for future studies on binary systems involving SC-CO₂. By providing a robust and detailed foundation, this review fosters a deeper appreciation of the complex interplay between CO₂ and various solutes, paving the way for more efficient and sustainable industrial processes. As the interest in SC-CO₂ continues to grow, the structured datasets and analyses presented here will remain a cornerstone for advancing research and applications in supercritical fluid technology.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/molecules31040614/s1>, Table S1: Compounds that are commonly used as SCF, and their critical properties. Table S2: Experimental phase equilibrium data of aliphatic hydrocarbon/CO₂ mixtures. Table S3: Experimental phase equilibria data of aromatic hydrocarbon/CO₂ mixtures. Table S4: Experimental phase equilibrium data of alcohol/CO₂ mixtures. Table S5: Experimental phase behaviour data of ether/CO₂ mixtures. Table S6: Experimental phase behaviour data of ester/CO₂ mixtures. Table S7: Experimental phase behaviour data of ketone/CO₂ mixtures. Table S8: Experimental phase behaviour data of water/CO₂ mixtures. Table S9: Experimental phase equilibrium data of monomer/CO₂ and polymer/CO₂ mixtures. Table S10: Experimental phase behaviour data of ionic liquids/CO₂ mixtures. Table S11: Experimental phase behaviour data of deep eutectic solvent/CO₂ mixtures.

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Abbreviations

B	Bubble Point
C	Critical Point
CCU	Carbon capture and utilization
CP	Critical Point
D	Dew Point
DES	Deep eutectic solvent
EOR	Enhanced Oil Recovery
HBA	Hydrogen Bond Acceptor
HBD	Hydrogen Bond Donor
IL	Ionic Liquid
L	Liquid
LA-LB	Lewis acid–Lewis base
LCEP	Lower Critical End Point
LLE	Liquid–Liquid Equilibria
MW	Molecular Weight
P	Pressure
PVT	Pressure–Volume–Temperature
PT	Pressure–Temperature
S	Solid
SC	Supercritical
SCF	supercritical fluid
T	Temperature
UCEP	Upper Critical End Point
V	Vapour
VLE	Vapour–Liquid Equilibria

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