

Bridging molecular interactions and macroscopic thermodynamics in deep eutectic solvents for CO₂ capture

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ABSTRACT

Deep eutectic solvents (DESs) offer a sustainable route to low-energy CO₂ capture owing to their tunable structure, low volatility, and recyclability. However, establishing clear relationships between molecular structure, thermophysical behaviour, and gas solubility remains essential for the rational design of next-generation DES-based capture systems. In this work, we integrate semi-empirical modeling with molecular dynamics (MD) simulations to describe the thermophysical properties and CO₂ solubility of three prototypical DESs—Reline, Glyceline, and Ethaline. A perturbed hard-sphere equation of state (PHS EoS) was applied to predict density, compressibility, and viscosity up to 100 MPa, while a revised μ - μ framework was used to correlate CO₂ solubilities over the temperature range 303–343 K. The PHS EoS provided accurate predictions of thermophysical properties, and the revised μ - μ model reproduced CO₂ solubilities with deviations below 10%. MD simulations revealed stable hydrogen-bond networks that promote CO₂ retention through a combination of physical and chemical interactions. Overall, this integrated and data-efficient approach bridges molecular-scale structure and macroscopic thermodynamics, providing a rational pathway for designing environmentally benign solvents for carbon capture and green separation processes.

1. Introduction

Deep eutectic solvents (DESs) are a class of sustainable, task-specific solvents that have attracted increasing attention as environmentally benign alternatives to conventional volatile organic solvents. Their appeal lies in their tunable composition, simple preparation, negligible vapor pressure, and potential biodegradability, making them suitable for a wide range of applications in green chemistry, biotechnology, and materials processing [1]. Typically, DESs are formed by mixing a hydrogen bond acceptor (HBA), such as a quaternary ammonium salt, with a hydrogen bond donor (HBD), such as an alcohol, acid, or amide. Strong hydrogen bonding between these components disrupts the crystal lattices of the individual species, producing an eutectic mixture with a melting point significantly lower than those of the pure constituents. This pronounced melting-point depression results in liquids that are often stable and fluid at room temperature, thereby offering low-cost, non-volatile alternatives to ionic liquids and other designer solvents [1].

Accurate knowledge of the thermophysical properties of DESs is essential for advancing their practical use, from laboratory-scale

synthesis to industrial applications. Properties such as density, viscosity, and isothermal compressibility determine how DESs perform in separation, extraction [2], and reaction systems. However, despite growing experimental interest, available thermophysical data remain limited and fragmented, often covering only narrow temperature and pressure ranges. The inherently high viscosity and hygroscopicity of DESs further complicate experimental measurements. Consequently, reliable predictive models are required to complement experimental observations, provide insights into molecular interactions, and guide the design of solvents with tailored physicochemical characteristics [3]. The development of accurate and computationally efficient tools for predicting these properties is therefore a key research objective.

Several approaches have been employed to describe the thermophysical behavior of DESs. Empirical and semi-empirical correlations [4–9], molecular dynamics (MD) simulations [10–13], and machine learning techniques [14–16] have all contributed to understanding the structure–property relationships of these complex liquids. Among these approaches, semi-empirical models remain particularly attractive because they combine physical interpretability with low computational

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cost. These models often include equations of state (EoS), group-contribution methods, or statistical thermodynamic approaches such as the conductor-like screening model for real solvents (COSMO-RS) [17–23]. Semi-empirical formulations enable both equilibrium properties (e.g., density) and non-equilibrium properties (e.g., viscosity) to be described using a limited number of fitted parameters with clear physical meaning, although their accuracy typically depends on the quality and range of the available data.

Molecular dynamics (MD) simulations, on the other hand, provide complementary microscopic insight. They enable direct observation of hydrogen bonding, molecular organization, and dynamic behavior at the atomic scale, thereby linking macroscopic properties to molecular structure [10–13]. By revealing the spatial distribution of ions, the lifetimes of hydrogen bonds, and local solvation structures, MD simulations play a crucial role in validating and interpreting macroscopic models. Together, semi-empirical equations and MD simulations offer a balanced framework: the former efficiently captures macroscopic thermodynamic trends, while the latter provides a molecular-level foundation for those trends.

Despite this progress, the high-pressure behavior of DESs remains poorly characterized. Most existing models are restricted to near-ambient conditions, resulting in a limited understanding of how these solvents respond to compression. High-pressure data are particularly relevant for applications in extraction, lubrication, catalysis, and gas absorption, where density, compressibility, and viscosity vary nonlinearly with pressure. Moreover, the solubility of gases such as CO₂ in DESs depends strongly on both pressure and molecular-level interactions. Predictive models capable of capturing these coupled effects are therefore needed to extend DES research to process-relevant conditions.

The present work addresses this challenge by combining semi-empirical modeling with molecular dynamics simulations to describe the high-pressure thermophysical properties and CO₂ solubility of ten representative DESs. A perturbed hard-sphere equation of state (PHS EoS) was developed and applied to correlate and predict density, compressibility, and viscosity over wide temperature (283–413 K) and pressure ranges (up to 100 MPa). The PHS EoS was further coupled with the revised μ - μ approach to model CO₂ solubility in selected DESs, capturing the balance between physical dissolution and weak chemical association. Complementary MD simulations provide atomistic insight into hydrogen-bond networks and solvation structures that stabilize CO₂ within the DES matrix.

This integrated approach establishes a consistent link between macroscopic thermophysical behavior and molecular-scale interactions. It also demonstrates that semi-empirical equations, when supported by molecular modeling, can reliably predict complex solvent behavior under extreme conditions. The outcomes of this study contribute to the rational design of deep eutectic solvents for low-energy CO₂ capture and other high-pressure separation processes.

2. Semi-empirical models for equilibrium and non-equilibrium properties

2.1. Perturbed hard-sphere EoS

The thermodynamic modeling framework employed in this work is based on the PHS equation of state, which combines the Carnahan-Starling hard-sphere term with a van der Waals perturbation accounting for attractive dispersion forces [24,25]. This formalism provides an optimal balance between physical rigor, computational efficiency, and practical applicability to complex associating fluids such as DESs. In terms of accuracy, simplicity, and applicability to different fluid systems, it is comparable to other EoS, including the Lennard-Jones [26], Peng-Robinson, and statistical associating fluid theory (SAFT) equations [27]. The compressibility factor, Z , is expressed as:

$$Z^{PHS} = Z_{CS}^{HS} + Z_{vdW}^{disp.} = \frac{P}{\rho k_B T} = 1 + b(T) \rho g(d^+) - \frac{a(T)}{k_B T} \rho \quad (1)$$

Here, P is the pressure in Pa, T is absolute temperature in K, ρ is the number density in mol·m⁻³ and $k_B T$ is the thermal energy per molecule in J. The term $g(d^+)$ denotes the pair radial distribution function of a hard-sphere fluid at contact, as given by the Carnahan-Starling equation [24], and can be expressed in terms of the packing fraction, y , as:

$$g(d^+) = \frac{(1 - y/2)}{(1 - y)^3} \quad (2)$$

$$\text{with } y = \frac{\pi \rho}{6} d^3 \quad (3)$$

This formulation accurately describes the structural ordering and pressure enhancement arising from molecular crowding, effects that become increasingly important at elevated pressures and in highly associated liquids such as DESs, where hydrogen bonding constrains molecular packing.

The temperature-dependent parameters $a(T)$ and $b(T)$ represent the attractive interaction strength and the effective covolume, respectively. These parameters are expressed in terms of two molecular quantities—the characteristic molecular diameter, d , and the well-depth energy, ϵ —through theoretically derived functional forms [28,29]:

$$a(T) = \frac{2\pi}{3} d^3 \epsilon F_a(T_r) \quad (4)$$

$$b(T) = \frac{2\pi}{3} d^3 F_b(T_r) \quad (5)$$

$$F_a(T_r) = a_1 \exp(-a_2 T_r) + a_3 \exp[-a_4 T_r^{3/2}] \quad (6)$$

$$F_b(T_r) = b_1 \exp(-b_2 T_r) + b_3 \exp[-b_4 T_r^{3/2}] \quad (7)$$

with empirically optimized coefficients: $a_1 = 1.058393$, $b_1 = 0.798019$, $a_2 = -0.879380$, $b_2 = 0.908086$, $a_3 = 0.609445$, $b_3 = 0.521304$, $a_4 = -0.314038$, $b_4 = -0.407266$.

For DES applications, the molecular parameters are determined separately for the HBA and HBD components and are then combined using physically motivated mixing rules:

$$\epsilon = \sqrt{\epsilon_{HBA} \epsilon_{HBD}} \quad (8)$$

$$d = \frac{d_{HBD} + d_{HBA}}{2} \quad (9)$$

The geometric mean used for the energy parameters reflects the scaling of London dispersion forces, while the arithmetic mean applied to the size parameters approximates the collision diameter. This component-based parametrization strategy enables the prediction of properties for previously untested DES formulations based on HBA and HBD parameters optimized against limited reference data—a crucial advantage for efficiently screening the vast compositional space of potential DES systems.

Although alternative schemes such as Wong and Sandler [30] and quadratic combining rules [31] are also available for property predictions, they introduce additional empirical parameters and coupling terms that reduce transparency. That is why the classical van der Waals one fluid mixing rules were employed, as they are mathematically consistent with its original formulation. They can provide reliable baseline behavior for asymmetric mixtures such as DESs as they are asymmetric in molecular volumes (e.g., CHCl₃ vs. urea) and interactions (ionic vs. H-bonding), however, both arithmetic and geometric means can be physically justified as arithmetic mean approximates the effective collision diameters in hard-sphere repulsion (Carnahan-Starling term), while geometric mean reflects the dispersive energy scaling.

It should be added that the molecular parameters (ϵ and d) for 5 HBD

and HBA constituents under study to be used in the PHS EoS were obtained by the simultaneous fitting of densities and isothermal compressibilities, for which the values were available in literature [32–39]. To do so, the following Objective Function (OF) was minimized by a least-squares method:

$$OF = \frac{100}{n} \sum_{i=1}^n \frac{|\rho^{Calc.} - \rho^{Exp.}|}{\rho^{Exp.}} + \frac{100}{n} \sum_{i=1}^n \frac{|\kappa_T^{Calc.} - \kappa_T^{Tait}|}{\kappa_T^{Tait}} \quad (10)$$

Then those optimized parameters were employed for 5 DESs using the mixing rules of Eqs. 8 and 9 to determine ε and d parameters of the rest of HBD and HBA constituents not included in the fit procedure mentioned above.

The PHS EoS provides analytical expressions for calculating derived thermodynamic properties using standard thermodynamic relations.

i) Isothermal compressibility:

$$k_T = - \left(\frac{1}{V} \right) \left(\frac{\partial P}{\partial V} \right)_T^{-1} = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T^{-1} \quad (11)$$

where V is the volume of the fluid system.

ii) Isobaric expansivity:

$$\alpha_P = - \left(\frac{1}{\rho} \right) \left(\frac{\partial \rho}{\partial T} \right)_P^{-1} \quad (12)$$

iii) Thermal pressure coefficient:

$$\gamma_V = \left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial P}{\partial T} \right)_\rho = \left(\frac{\alpha_P}{k_T} \right) \quad (13)$$

iv) Discrepancy of isobaric and isochoric molar heat capacities:

$$C_P - C_V = \left(\frac{\alpha_P^2 T}{\rho \kappa_T} \right) \quad (14)$$

This difference provides valuable insight into the thermal behavior of fluids and offers a useful metric for its quantitative characterization. Moreover, understanding the distinction between C_P and C_V is crucial for assessing the reliability and accuracy of thermodynamic models. For DESs, this difference is expected to be anomalously small due to the constrained molecular environment imposed by extensive hydrogen bonding, in which volume expansion against intermolecular attractions (relevant to C_P) is strongly limited, rendering isobaric and isochoric processes nearly equivalent. Accurate prediction of this subtle difference therefore serves as a stringent test of EoS quality for highly associated liquids.

2.2. High-pressure CO₂ solubilities

Over the past few years, DESs have been increasingly recognized as promising solvents for CO₂ capture, as they often exhibit enhanced CO₂ solubility compared to conventional solvents. Consequently, the measurement, correlation, and prediction of CO₂ solubility in DESs are crucial for the design and optimization of CO₂ capture processes employing these novel solvents [40,41]. In this work, the capability of the PHS EoS is further explored, with the inclusion of a binary interaction parameter, to correlate high-pressure CO₂ solubilities in three selected DESs: Reline, Glyceline, and Ethaline. To this end, the well-established μ - μ approach, based on the phase equilibrium criterion for the chemical potential of CO₂ in both liquid and vapor phases, was adopted [42]:

$$\mu_i^l = \mu_i^v \quad (15)$$

$$A_i^l = A_i^v + \frac{P_i^s}{\rho_i^s} \quad (16)$$

Here, A_i^l denotes the partial molar Helmholtz free energy of

component i in the liquid phase, which corresponds to the chemical potential of that component in liquid mixture. The expression for A_i^l , derived from the Helmholtz free energy function A_{ij} , is given as [42]:

$$\mu_i^l = A_i^l = \left(\frac{\partial A_{ij}}{\partial n_i} \right)_{T, \rho, j \neq i} \quad (17)$$

Here, the superscripts l and v denote the thermodynamic functions of CO₂ in the liquid and vapor phases, respectively, and P_s represents the equilibrium pressure at which CO₂ dissolves in the DESs of interest. Given an EoS, the Helmholtz free energies of CO₂ in both the liquid and vapor phases, as well as the chemical potential of CO₂ in the liquid phase, can be evaluated.

However, direct application of Eq. (15) consistently resulted in average absolute relative deviations (AARDs) exceeding 100% for CO₂ solubilities in all investigated DESs, indicating a fundamental inadequacy of the standard formulation. This failure likely arises from the treatment of hydrogen bonding within the PHS EoS as isotropic dispersion interactions rather than as directional and saturable associations. As a result, strong and specific CO₂-DES interactions—particularly those involving the quadrupole moment of CO₂ and the hydroxyl or amine groups of the DES components—are not adequately captured by simple geometric mixing rules.

Following the approach proposed by Chen et al. [43], a theoretical revision to Eq. 15 was therefore implemented, rather than modifying the expressions for the liquid-phase Helmholtz free energy derived from the PHS EoS. This modification is necessary because the original formalism (Eq. 15) fails to predict CO₂ solubilities in the studied DESs, as evidenced by the large AARD values (>100%). Accordingly, the general phase equilibrium criterion was reformulated as:

$$\mu_i^l = \phi(\rho^*) \mu_{i,EoS}^l = \mu_i^v \quad (18)$$

Here, the subscript *EoS* denotes the chemical potential determined from the present PHS EoS, and $\phi(\rho^*)$ is a reduced density-dependent correction factor applied to the chemical potential of CO₂ in the liquid phase. In fact, it modifies the chemical-potential balance to account for association and density effects. From a molecular perspective, the correction reflects the influence of local packing and association environments on the chemical potential of CO₂, which are not fully captured by a purely hard-sphere-based treatment. Then is not derived from a molecular simulation or microscopic considerations as it is a semi-empirically derived equation for some typical DES/CO₂ system and then extended to other studied DES/CO₂ systems.

To proceed with the calculation of CO₂ solubilities, the mixture formulation of the PHS EoS is provided in the [Supplementary Material](#), including the combining rules for the temperature-dependent parameters $b(T)$ and $a(T)$, as well as a binary interaction parameter, k_{ij} , for the cross-dispersive energy parameter, $a_{ij}(T)$. The numerical values of this binary interaction parameter are commonly reported for solvent-gas systems at a given isotherm; however, it has been shown that k_{ij} exhibits a noticeable temperature dependence [44].

2.3. Correlation and prediction of non-equilibrium properties: viscosity

2.3.1. Rough hard-sphere theory (RHST)

Viscosity modeling was performed using the RHST theory, an extension of the modified Enskog theory that accounts for molecular rotational coupling and non-spherical shape effects [45–49]. In terms of reduced viscosity, η^* is expressed as follow [45]:

$$\eta_{RHS}^* = C_\eta \frac{d^2}{\sqrt{N_A^{-1} M_w \epsilon}} \eta_{SHS} \quad (19)$$

Here, M_w is the molecular weight (g·mol^{−1}), N_A is Avogadro's number (mol^{−1}), and η_{SHS} is the dynamic viscosity (Pa·s) of a smooth hard-sphere fluid, as defined by Dymond [46,47,50], and is closely

related to the compressibility factor of the hard-sphere fluid according to the modified Enskog theory. The quantity η^* denotes the reduced viscosity of a rough hard-sphere fluid according to Ref. [45], and C_η is the roughness factor, which is expressed in terms of the reduced pressure ($P_r = P/0.1$ MPa) and reduced temperature ($T_r = k_B T/\epsilon$) [45]:

$$C_\eta = F_\eta e^{(\omega(T_r)(P_r-1))} \quad (20)$$

With

$$F_\eta = (c_1 + c_2 T_r)^{-(1/c_3)} \quad (21)$$

Here, c_1 – c_3 are fitting coefficients of the RHST model, whose values were adjusted using viscosity data at 0.1 MPa, as reported in Table S3 of the Supplementary Material for the studied DESs.

In Eq. 20, ω is a universal function of the reduced temperature, expressed as follows:

$$\omega(T_r) = -5.7537 \times 3 T_r + 1.186 \times 10^{-3} \quad (22)$$

Accordingly, the model is predictive for pressures higher than 0.1 MPa, as Eq. 22 is universal and the fitting procedure for Eq. 21 was based solely on data at 0.1 MPa.

2.3.2. Eyring Rate Theory (ERT)

The ERT theory interprets viscous flow as an activated process in which molecules overcome energy barriers to exchange positions [51]. In this framework, the activation energy for viscous flow is treated as a thermodynamic free energy. The viscosity of the system is described as the sum of a reference term, η_0 , given by Eq. 24, and a contribution derived from the residual Helmholtz free energy of the system, which accounts for deviations from the viscosity behavior of a non-attracting rigid sphere model, as expressed below [52]:

$$\ln \eta_{ERT} = \ln \eta_0 - \left(\frac{A^{res}}{R T} \right) \quad (23)$$

With

$$\ln \eta_0 = \chi(T_r) \ln \left(\frac{\beta(\rho^*) d^2}{\sqrt{N_A^{-1} M_w \epsilon}} \right) \quad (24)$$

Here, A^{res} is the residual Helmholtz free energy of the fluid at given T and P , and $\beta(\rho^*)$ and $\chi(T_r)$ are, respectively, characteristic linear functions of the reduced density ($\rho^* = \rho d^3$) and reduced temperature ($T_r = k_B T/\epsilon$) defined as:

$$\beta(\rho^*) = w_1 \rho^* + w_2 \quad (25)$$

$$\chi(T_r) = s_1 * T_r + s_2 \quad (26)$$

Here, w_1 – s_3 are the fitting coefficients of the ERT-based model, whose values are reported in Table S4 of the Supplementary Material for the studied DESs.

2.4. Molecular dynamics simulations

Molecular dynamics simulations were performed using the MDyna-Mix v.5.3 package [53], with force field parameters derived from the Merck Molecular Force Field through the SwissParam database [54]. Atomic partial charges were computed using the ChelpG method [55], applied to DFT-optimized monomer geometries, ensuring consistent electrostatic representations. Details of the force field parametrization are provided in Table S1 (Supplementary Material).

Two simulation protocols were employed: (i) pure DES systems to characterize bulk liquid structure and thermodynamics, and (ii) DES/CO₂ interfaces to probe gas capture mechanisms. Initial configurations were generated using Packmol software [56] to achieve random molecular arrangements in cubic simulation boxes, with system compositions detailed in Table S2 (Supplementary Material). Simulations

spanned 293–353 K and 0.1–60 MPa, encompassing typical CO₂ capture operating conditions.

Each simulation followed a three-stage equilibration and production protocol: (i) 1 ns NVT (isochoric-isothermal) simulation at the target temperature to equilibrate kinetic energy distributions, (ii) 10 ns NPT (isothermal-isobaric) equilibration at each pressure-temperature condition to achieve steady-state density and remove initial configuration artifacts, and (iii) 100 ns NPT production runs for statistical sampling of equilibrium properties. The extended production period (significantly longer than typical DES relaxation times of ~ 1 – 10 ns) ensures convergence of structural correlation functions and ensemble averages. Temperature and pressure control employed the Nosé-Hoover thermostat and barostat [57], with coupling constants optimized to maintain stable trajectories while allowing natural fluctuations characteristic of the NPT ensemble.

Equations of motion were integrated using the Tuckerman-Berne double time-step algorithm [58] with 1 fs outer steps for non-bonded forces and 0.1 fs inner steps for intramolecular vibrations, providing efficient integration while maintaining energy conservation to within 0.01% over 100 ns trajectories. Long-range electrostatic interactions were computed via Ewald summation [59] with 10 Å real-space cutoff and automatic reciprocal-space convergence criteria, ensuring accurate treatment of the strong ionic interactions in Type III DESs. Lennard-Jones potentials were truncated at 15 Å with analytical tail corrections applied. Cross-interaction parameters employed Lorentz-Berthelot combining rules: arithmetic mean for size parameters, geometric mean for energy parameters.

Trajectory analysis utilized TRAVIS (Trajectory Analyzer and Visualizer) [60] and VMD (Visual Molecular Dynamics) [61] software packages to compute radial distribution functions (RDFs), spatial distribution functions (SDFs), combined distribution functions (CDFs), coordination numbers, hydrogen bond populations, and interaction energies. Hydrogen bonds were identified using geometric criteria: donor-acceptor distance ≤ 3.5 Å and hydrogen-donor-acceptor angle $\leq 60^\circ$, consistent with literature standards for associated liquids. These criteria capture the directional, relatively short-range nature of hydrogen bonding while excluding weaker, non-specific interactions.

The force field validation strategy involved comparing predicted densities with experimental measurements, with deviations of 2–4% considered acceptable for classical, non-polarizable force fields. This level of accuracy indicates that the essential physics—molecular sizes, charge distributions, and interaction strengths—are adequately captured, enabling a reliable investigation of structural properties and interaction mechanisms, which are less sensitive to the quantitative accuracy of the force field than absolute thermodynamic properties.

3. Results & discussion

3.1. Semiempirical modeling of thermodynamics properties

As described earlier, the two molecular parameters of the PHS equation of state—the energy parameter (ϵ) and the molecular diameter (d)—were optimized to capture the specific roles of the HBD and HBA components in each DES. These parameters were adjusted by fitting experimental density and isothermal compressibility data (κ_T). Table 1 presents the optimized molecular parameters, along with the AARDs obtained from fits to experimental densities [32–39] and from the Tait-type equations reported in the literature [33–35]. For several systems, including decanoic acid, dodecanoic acid, reline, ethaline, glycerine, and glycerol, the reference κ_T values ($\kappa_{T,Tait}$) were taken from Tait-type equations. The corresponding correlation coefficients and detailed AARDs are provided in the Supplementary Material (Table S5).

The results in Table 1 show that the PHS EoS reproduces both density and κ_T over a wide temperature (283–413 K) and pressure (up to 100 MPa) range with satisfactory accuracy. The overall AARDs, calculated from 1268 data points, were 0.27% for density and 3.14% for κ_T .

Table 1

Optimized molecular parameters for HBD and HBA components, along with the AARDs^{a,b} (in %) for correlated densities and isothermal compressibilities of the studied DESs using the PHS EoS.

DES	$\varepsilon_{\text{HBA}}/k_B$	$d_{\text{HBA}}(\text{nm})$	$\varepsilon_{\text{HBD}}/k_B$	$d_{\text{HBD}}(\text{nm})$	$\Delta P(\text{MPa})$	$\Delta T(\text{K})$	NP ^c	AARD ^a %	AARD ^b %	Ref.
HBA:HBD										
[Ch]Cl:EG (1:2)	3385.1	0.55673	1673.5	0.43231	0.1–95	283–363	216	0.04	1.83	[32]
[Ch]Cl:Urea(1:1)	3385.1	0.55673	2054.2	0.40933	0.1–95	293–363	192	0.09	2.03	[32]
Menthol:Oct(1:1)	2271.4	0.64827	1891.0	0.61759	0.1–60	293–413	154	0.95	7.53	[33]
Cam:Menthol (1:2)	2061.6	0.62380	2271.4	0.64827	0.1–65	283–338	192	0.39	3.26	[34]
Cam:Thymol (1:1)	2061.6	0.62380	2433.3	0.61654	0.1–65	283–338	192	0.29	2.46	[34]
Compound										
Ethylene glycol		ε/k_B	$d(\text{nm})$		$\Delta P(\text{MPa})$	$\Delta T(\text{K})$	NP ^b	AARD%	AARD%	Ref.
Glycerol	1673.5	0.43231			0.1–45	283–323	90	0.04	1.26	[35]
Octanoic acid	2485.70	0.48404			0.1–100	278–323	90	0.14	3.97	[36,37]
Decanoic acid	1891.0	0.61759			0.1–25	293–323	70	0.24	4.01	[38]
Decanoic acid	1673.5	0.43231			0.1–9	343–373	36	0.30	2.91	[39]
Decanoic acid	1673.5	0.43231			0.1–9	343–373	36	0.30	2.91	[39]
Dodecanoic acid	2433.9	0.70789			0.1–9	343–373	36	0.31	3.57	[39]
Overall							1268	0.27	3.14	

$$^a \text{ARD} = \frac{100}{NP} \sum_{i=1}^{NP} \frac{|\rho^{\text{Calc.}} - \rho^{\text{Exp.}}|}{\rho^{\text{Exp.}}}$$

$$^b \text{ARD} = \frac{100}{n} \sum_{i=1}^n \frac{|\kappa_T^{\text{Calc.}} - \kappa_T^{\text{Tait}}|}{\kappa_T^{\text{Tait}}}$$

^c NP represents the number of data points examined

relative to the experimental and Tait-type data [32–39]. These results indicate that the PHS model can effectively describe the compressibility and volumetric behavior of DESs using a small number of molecular parameters. The optimized ε and d values reflect, in an averaged sense, the balance between repulsive molecular packing and attractive hydrogen-bonding interactions characteristic of DESs. The ability of such a simple equation to represent complex solvent systems across broad conditions demonstrates that the essential thermodynamic trends are well captured.

The predictive capability of the PHS EoS was then tested for five DESs not included in the fitting stage. Table 2 summarizes the AARDs for predicted densities and κ_T values obtained for 1272 data points over 283–413 K and pressures up to 95 MPa, compared with experimental and Tait-type data [32,34,62–65]. The model predicted both properties with overall deviations of 1.30% and 5.44%, respectively, confirming

Table 2

AARDs^{a,b} (in %) of predicted densities and κ_T for the studied DESs using the PHS EoS, based on the HBD and HBA contributions to the molecular parameters.

DES	ΔP (MPa)	$\Delta T(\text{K})$	NP ^c	AARD ^a %	AARD ^b %	Ref.
HBA:HBD						
[Ch]Cl:Gly (1:2)	0.1–95	283–363	216	1.71	3.60	[32]
	0.1–50	298–323	66	1.92	8.08	[62]
	0.1–65	283–338	192	1.53	5.06	[34]
[Ch]Cl:EG (1:2)	0.1–65	283–338	192	0.13	3.95	[34]
	0.1–50	298–323	66	0.03	1.14	[63]
[Ch]Cl:Urea (1:1)	0.1–50	298–323	66	0.22	7.27	[64]
Menthol:Dca (1:1)	0.1–60	293–413	154	1.11	7.49	[33]
Menthol:Dodca (2:1)	0.1–45	303–413	110	3.12	7.74	[33]
Menthol:Thymol (2:1)	0.1–60	293–353	56	0.45	4.75	[65]
Dodca:Oct(1:3)	0.1–60	293–413	154	2.05	7.35	[33]
Overall			1272	1.30	5.55	

$$^a \text{ARD} = \frac{100}{NP} \sum_{i=1}^{NP} \frac{|\rho^{\text{Calc.}} - \rho^{\text{Exp.}}|}{\rho^{\text{Exp.}}}$$

$$^b \text{ARD} = \frac{100}{n} \sum_{i=1}^n \frac{|\kappa_T^{\text{Calc.}} - \kappa_T^{\text{Tait}}|}{\kappa_T^{\text{Tait}}}$$

^c NP represents the number of data points examined

that the molecular parameters derived in the fitting stage are transferable and can be used to estimate properties for other DESs with reasonable accuracy. Only a few systems—Menthol:Dodecanoic acid (2:1), Dodecanoic acid:Octanoic acid (1:3), and choline chloride-glycerol (ChCl:Gly) (1:2)—showed higher AARD values (above 1.5%). In these cases, the aliphatic nature of one or both components appears to reduce model accuracy. Longer hydrocarbon chains lower polarity and weaken the hydrogen bonding network, making the fluids less compact and more difficult to describe using a hard-sphere-based equation. This trend aligns with the general observation that models based on polar interaction assumptions are less accurate for DESs dominated by dispersive forces. The increase in viscosity deviations with longer aliphatic chains can be attributed to structural and dynamic heterogeneity within the DES matrix. As the hydrogen bond donor or acceptor becomes more aliphatic, the system exhibits stronger van der Waals interactions and reduced hydrogen-bond density, resulting in less homogeneous molecular packing. These effects amplify local microstructural fluctuations and hinder collective molecular mobility, making viscosity more sensitive to subtle inaccuracies in the fitted molecular parameters of the EoS. Consequently, longer-chain DESs exhibit stronger non-ideal behavior and greater uncertainty in viscosity predictions compared with systems containing short, polar components that form more uniform hydrogen-bonded networks.

To further evaluate model performance, the results were compared with those from the volume translation (VT) equations of state—namely, volume translated Soave-Redlich-Kwong (VT-SRK) and volume translated Peng-Robinson (VT-PR)—reported in Ref. [8]. As shown in Table 3, the PHS EoS achieved an average AARD of 0.63% for 822 data points, which is comparable to the accuracy of VT-SRK (0.80%) and VT-PR (0.46%). For most systems, the PHS predictions were within the same error range as the VT-based EoSs. The main distinction is that the PHS model provides predictive results, whereas the VT-SRK and VT-PR methods require refitting a volume correction parameter for each temperature and pressure range. This difference is significant, as it indicates that the PHS equation can achieve similar reliability without additional empirical correction terms. Consequently, it captures the key physical balance between molecular repulsion and attraction without relying on fitted volume translations.

Table 4 presents the results for two derived thermodynamic properties—the isobaric thermal expansion coefficient (α_p) and the isochoric thermal pressure coefficient (γ_V)—predicted for five DESs using the PHS EoS. The equation predicted α_p and γ_V values over the range 283–363 K

Table 3

Comparison of the AARDs^a (in %) of correlated and predicted densities for selected DESs using the PHS EoS (this work) with VT-SRK and VT-PR EoSs from Ref. [8] based on experimental measurements.

Compound	ΔP (MPa)	ΔT (K)	NP ^b	This work ^a	VT- SRK ^a	VT- PR ^a	Data Source
HBA:HBD							
[Ch]Cl:Gly (1:2)	0.1–95	283–363	282	1.75	0.56	0.27	[32]
[Ch]Cl:EG (1:2)	0.1–95	283–363	282	0.04	0.93	0.55	[32]
[Ch]Cl: Urea(1:1)	0.1–95	293–363	258	0.12	0.91	0.56	[32]
Overall			822	0.63	0.80	0.46	

$$^a \text{ARD} = \frac{100}{NP} \sum_{i=1}^{NP} \left| \frac{\rho^{\text{Calc.}} - \rho^{\text{Exp.}}}{\rho^{\text{Exp.}}} \right|$$

^b NP represents the number of data points examined

Table 4

AARDs^{a,b} (in %) of predicted α_p and γ_V for selected DESs using the PHS EoS (this work), compared with values obtained from Tait-type equations reported in the literature.

DES	ΔP (MPa)	ΔT (K)	NP ^c	AARD% ^a	AARD% ^b
HBA:HBD					
[Ch]Cl:EG (1:2)	0.1–95	283–363	216	4.75	5.45
	0.1–65	283–338	192	8.42	7.29
	0.1–50	298–323	66	7.53	6.46
[Ch]Cl:Urea(1:1)	0.1–50	298–323	66	15.36	14.24
	0.1–95	293–363	192	10.47	11.04
[Ch]Cl:Gly (1:2)	0.1–95	283–363	216	7.05	9.77
	0.1–50	298–323	66	11.02	8.94
	0.1–65	283–338	192	7.32	12.20
Cam:Thymol (1:1)	0.1–65	283–338	192	26.30	27.15
Menthol:Thymol (2:1)	0.1–60	293–353	56	12.88	13.03
Overall			1454	10.72	11.70

$$^a \text{ARD} = \frac{100}{NP} \sum_{i=1}^{NP} \left| \frac{\alpha_p^{\text{Calc.}} - \alpha_p^{\text{Tait}}}{\alpha_p^{\text{Tait}}} \right|$$

$$^b \text{ARD} = \frac{100}{NP} \sum_{i=1}^{NP} \left| \frac{\gamma_V^{\text{Calc.}} - \gamma_V^{\text{Tait}}}{\gamma_V^{\text{Tait}}} \right|$$

^c NP represents the number of data points examined

and up to 95 MPa, with overall AARDs of 10.72% and 11.70%, respectively, for 1454 data points. These deviations are acceptable when compared with those reported for ionic liquids using SAFT-based EoSs in Ref. [66], which ranged from 6.72% to 71.23% for α_p predictions. Considering that DESs are polar fluids with strong directional interactions, errors around 11% for the derived quantities are reasonable and confirm that the model maintains internal consistency across different thermodynamic properties. The results also demonstrate that once the density behavior is well represented, related properties such as α_p and γ_V can be reliably predicted using the same molecular parameters.

The behavior of the heat capacity difference ($C_p - C_V$) was also examined to assess the model's thermodynamic consistency under pressure. Fig. 2 shows ($C_p - C_V$) as a function of pressure for Glyceline at 283.15, 323.15, and 343.15 K. Open symbols represent values calculated from the Tait-type equation (Supplementary Material), while filled symbols represent predictions from the PHS EoS. Both approaches indicate that ($C_p - C_V$) remains small and nearly constant with pressure, reflecting the limited molecular rearrangement possible in these dense liquids. The absolute differences between the two methods—0.051 and 0.071 J·mol⁻¹·K⁻¹—are minimal, demonstrating good agreement between the PHS and Tait-type formalisms.

The temperature dependence of ($C_p - C_V$) shows a slight decrease with temperature in the PHS EoS results, whereas the Tait-type equation

predicts a weak increase. This difference can be attributed to the opposite temperature trends of α_p : in the PHS model, α_p decreases with temperature, while in the Tait-type approach it increases. The PHS prediction suggests that the liquid's expansion ability diminishes as thermal motion disrupts the hydrogen bond network, leading to denser molecular packing. Although both methods yield consistent magnitudes, this subtle difference highlights how model assumptions influence secondary thermodynamic predictions.

Overall, the PHS EoS provides a reliable and physically grounded approach for describing the volumetric and related thermodynamic properties of DESs under high pressure. It performs comparably to more complex equations of state, but with far fewer adjustable parameters and no need for system-specific fitting. The model accurately reproduces the main experimental trends in density, compressibility, and derived coefficients, making it suitable for both engineering and molecular modeling applications. The results also confirm that the predictive capability of the PHS EoS depends on the balance of polarity and hydrogen bonding within the solvent pair, which governs molecular packing and compressibility. In this context, the PHS EoS serves as a practical predictive tool for estimating the high-pressure properties of DESs, particularly when experimental data are scarce or difficult to obtain.

Despite Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) [27] and Cubic Plus Association (CPA) [67] EoS models are important reference EoS models for associating fluids, the present PHS framework is simpler, requires fewer adjustable parameters, and is easier to implement for screening large sets of DES compositions. However, its limitation is that it does not include explicit association terms, so it can not represent site-specific hydrogen bonding at the same microscopic level as PC-SAFT or CPA can so.

3.2. Semiempirical modelling of viscosity

The predictive and correlative capabilities of the RHST and ERT models were evaluated for the viscosity of three representative DESs, for which reliable experimental data are available in the literature [32]. The experimental datasets cover a wide pressure range, from near-ambient conditions (0.1 MPa) up to 100 MPa, allowing a thorough assessment of the models under both low- and high-pressure regimes. The performance of the RHST- and ERT-based models was compared with that of friction theory (FT)-based approaches reported in Ref. [8], specifically the VT-SRK+FT and VT-PR+FT combinations. Table 5 summarizes the AARDs (in %) obtained for both correlation and prediction tests.

As shown in Table 5, both semi-empirical models developed in this work reproduced the experimental viscosities of the studied DESs with good accuracy across the entire pressure range. For the 148 data points examined, the RHST- and ERT-based models achieved overall AARDs of 5.45% and 3.73%, respectively. The ERT-based formulation therefore provided the best agreement with experiment among all the methods tested. Although the RHST-based model produced slightly larger deviations, it is worth noting that its results represent *true predictions* beyond the calibration range (pressures above 0.1 MPa), whereas the ERT-based and VT-based models were correlated over the full dataset. This distinction highlights the stronger transferability of the RHST approach despite its simpler formalism. Nevertheless, the ERT-based model demonstrated superior overall correlation capability, outperforming both the VT-SRK+FT and VT-PR+FT models reported in Ref. [8] in terms of accuracy and consistency across temperatures and pressures.

To illustrate how the proposed models reproduce the experimental data, Figs. 3a–3c show the variation of viscosity with pressure for Ethaline (Fig. 3a), Reline (Fig. 3b), and Glyceline (Fig. 3c) along several isotherms. In these figures, open symbols correspond to experimental viscosity data from the literature [32], solid lines represent the ERT-based model predictions, and dashed lines correspond to the RHST-based results. Overall, the agreement between the models and

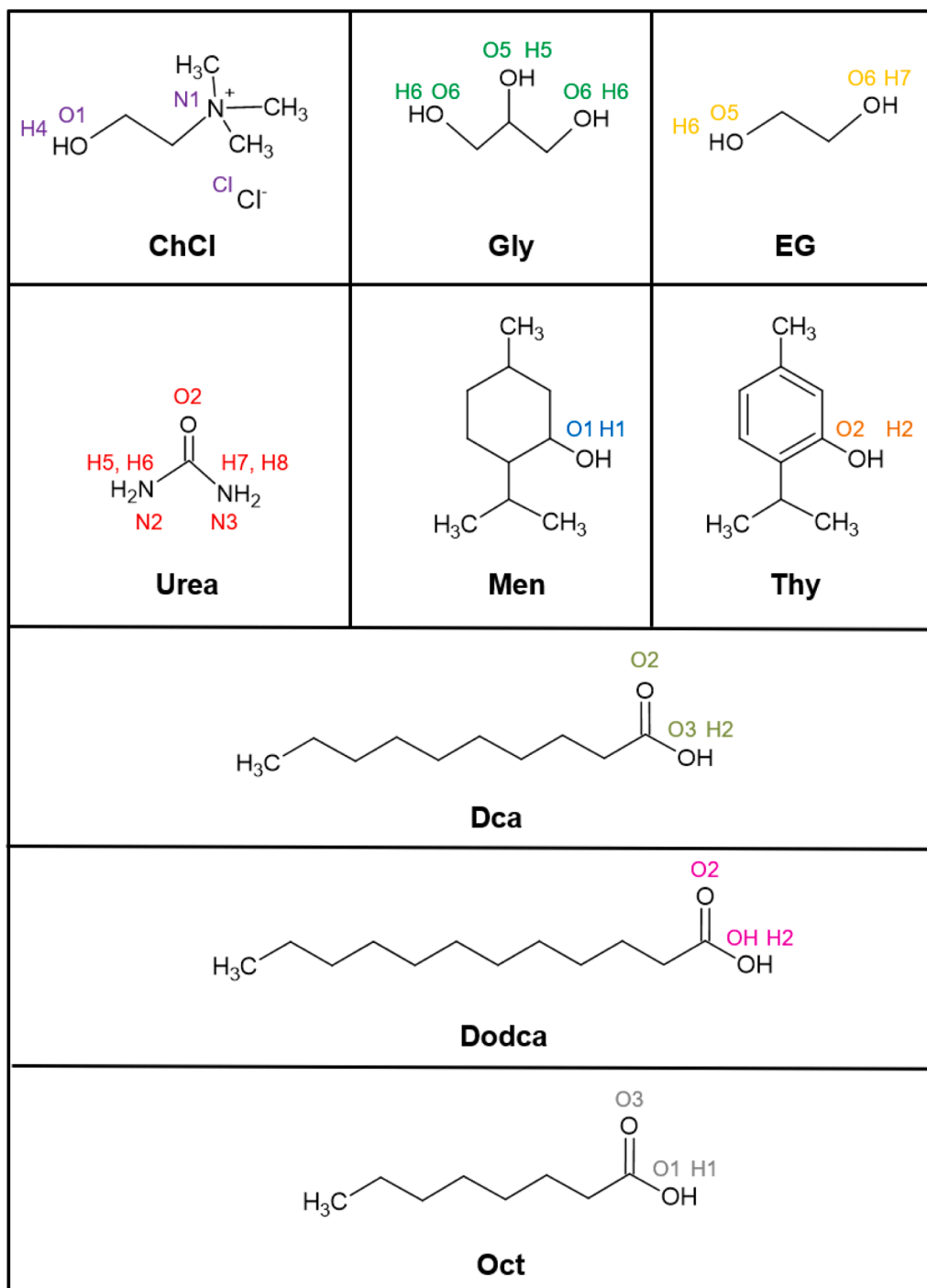


Fig. 1. Molecular structures of the compounds used in this work and the developed DESs.

experiment data is satisfactory across the investigated pressure and temperature ranges. A closer inspection of Figs. 3a–3c reveals that the predictive accuracy of the RHST-based model gradually decreases at higher pressures, particularly along the 313.15 K isotherms. This behavior likely arises from the simplified treatment of molecular roughness and collisional dynamics in the RHST approach, which becomes less representative as pressure increases and molecular packing effects become more pronounced. In contrast, the ERT-based model, which explicitly incorporates activation energy and molecular mobility through the rate-theory framework, remains accurate across the entire pressure range. This performance indicates that the viscosity behavior of DESs under compression is more accurately described when dynamic

processes—such as hydrogen-bond rearrangement of and short-range diffusion barriers—are explicitly accounted for, as in the ERT model.

Overall, both models captured the non-linear dependence of viscosity upon compression that reflects reduced free volume and stronger intermolecular coupling. The ERT-based model, in particular, reproduced the curvature and slope of the experimental trends with minimal deviation. Its ability to describe viscosities at both low and high pressures suggests that the ERT formalism captures the essential balance between molecular activation processes and volume constraints inherent to DESs.

Therefore, the RHST and ERT models provide a simple but physically

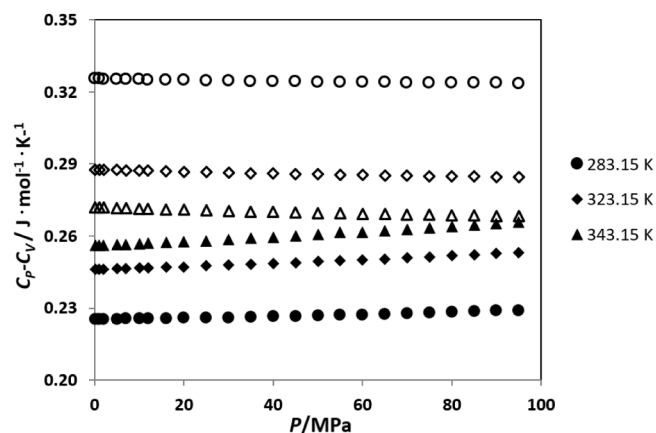


Fig. 2. Variation of $C_p - C_v$ with pressure for Glyceline at several isotherms: 283.15 K, 323.15 K, and 343.15 K. Open markers correspond to values obtained from the Tait-type equation in the [Supplementary Material](#), while filled markers represent predictions from the PHS EoS.

meaningful approach for estimating the viscosity of DESs over wide pressure ranges. The RHST formulation offers a predictive framework that can be applied without refitting, whereas the ERT-based model delivers higher overall accuracy and better agreement with experimental data. Compared with the more complex VT-SRK+FT and VT-PR+FT approaches [8], the present models achieve comparable or superior performance with fewer parameters and a clearer physical interpretation. These results demonstrate that semi-empirical formulations grounded in molecular theory can effectively describe the viscous behavior of DESs, bridging the gap between macroscopic measurements and the microscopic mechanisms of molecular motion and hydrogen bonding that govern resistance to flow. The observed increase in viscosity deviations for DESs with longer aliphatic chains likely arises from enhanced van der Waals interactions and reduced molecular mobility, which amplify non-ideal packing effects at elevated pressures.

3.3. MD modelling of DESs as a function of pressure and temperature

MD simulations provide atomistic insight into the structural origins of the macroscopic properties described above. Fig. 4 presents MD-predicted densities for seven DES systems at two temperatures (293 and 353 K) and four pressures (0.1, 10, 30, and 60 MPa). The simulations reproduce the expected density hierarchy: Type III DESs (ChCl-based) exhibit densities in the range of 1.15–1.27 g·cm⁻³, whereas Type V DESs (menthol-based) show lower values of 0.88–1.05 g·cm⁻³. Comparison with experimental literature data (0.85–1.25 g·cm⁻³) [33, 68–73] reveals a systematic overprediction of 2–4%, which is an acceptable deviation for fully predictive classical force-field simulations and validates the chosen parametrization strategy. This overprediction likely stems from a slight underestimation of thermal fluctuations

and/or the absence of explicit polarization effects in the fixed-charge model.

In addition to density, the center-of-mass self-diffusion coefficients (D), reported in Table 6, were determined from the slope of the Mean Square Displacements (MSD) (Figure S1) using Einstein's equation, providing further insight into the dynamical behavior of the DES systems and offering complementary validation of the force field. According to the Stokes-Einstein (SE) relation, diffusion is inversely proportional to viscosity, and therefore consistent trends between both properties are expected if the molecular interactions are properly captured. As shown in Table 6, DESs exhibiting higher experimental viscosities (e.g., ChCl:Gly, Fig. 3) systematically display lower diffusion coefficients, whereas less viscous systems such as Men:Thy present significantly higher diffusivities. Intermediate systems such as Men:Dca follow the same trend, confirming a coherent inverse relationship between D and viscosity across the studied DESs. This agreement indicates that the force field is able to reproduce not only static structural properties but also transport behavior governed by intermolecular friction. The temperature dependence of D further supports this validation. Increasing temperature leads to a systematic increase in diffusion coefficients, which is consistent with the experimentally observed decrease in viscosity for DESs. This behavior reflects the progressive weakening of hydrogen-bond networks and enhanced molecular mobility, confirming that the force field captures the balance between cohesive interactions and thermal motion. Pressure effects are comparatively moderate, in agreement with the relatively small experimental variations in viscosity under compression, suggesting that the underlying interaction network remains largely intact within the investigated pressure range. Overall, the consistency between MD-derived diffusion coefficients and experimental viscosity trends provides strong evidence that the employed force field reliably describes both structural and dynamical aspects of DESs. This combined validation strengthens the connection between molecular-level simulations and macroscopic transport properties, addressing a key requirement for bridging scales in these systems.

Consistently with these dynamical observations, temperature effects on density are also pronounced and systematic: density decreases of 4–6% occur upon heating from 293 to 353 K, corresponding to thermal expansion coefficients of $6\text{--}8 \times 10^{-4} \text{ K}^{-1}$. Choline chloride-urea (ChCl:Urea) exhibits the greatest temperature sensitivity, whereas dodecanoic acid-octanoic acid (Dodca:Oct) shows the smallest, reflecting differences in hydrogen-bond network rigidity. Pressure effects are more modest but systematic, with approximately linear density increases of 2–3% from 0.1 to 60 MPa, indicating compressibilities of 0.3–0.5 GPa⁻¹. The relatively low compressibility, particularly for ChCl-based systems, underscores their structural robustness arising from strong hydrogen-bond networks that resist mechanical compression.

Radial distribution functions (RDFs) provide direct evidence of intermolecular structure. Figs. 5 and 6 present HBA-HBD pair RDFs at 293 and 353 K over the investigated pressure range. For ChCl-based DESs (panels a-c), the Cl...H (hydroxyl/amine) RDFs display sharp first peaks at 2.0–2.2 Å, with intensities of $g(r)_{\text{max}} = 4\text{--}6$, characteristic

Table 5

Comparison of the AARDs^a (in %) of correlated and predicted viscosities obtained using the RHST- and ERT-based models (this work) with those from FT-based models reported in Ref. [8], including VT-SRK+FT and VT-PR+FT. For three of the investigated models (ERT, VT-SRK+FT and VT-PR+FT), the results were correlated over the entire pressure range, whereas the RHST-based model provided predictions for pressures above 0.1 MPa.

Compound	ΔP (MPa)	ΔT (K)	NP ^b	RHST ^a	ERT ^a	VT-SRK+FT ^a	VT-PR+FT ^a	Data Source
HBA:HBD								
[Ch]Cl:Gly (1:2)	0.1–100	293–373	51	7.02	3.02	3.58	3.00	[32]
[Ch]Cl:EG (1:2)	0.1–100	293–393	53	3.35	2.67	2.25	2.45	[32]
[Ch]Cl:Urea(1:1)	0.1–100	293–373	44	6.43	5.83	8.66	8.36	[32]
Overall		148	5.45	3.73	4.61	4.39		

$$^a \text{AARD} = \frac{100}{NP} \sum_{i=1}^{NP} \frac{|\eta^{\text{Calc.}} - \eta^{\text{Exp.}}|}{\eta^{\text{Exp.}}}$$

^b NP represents the number of data points examined

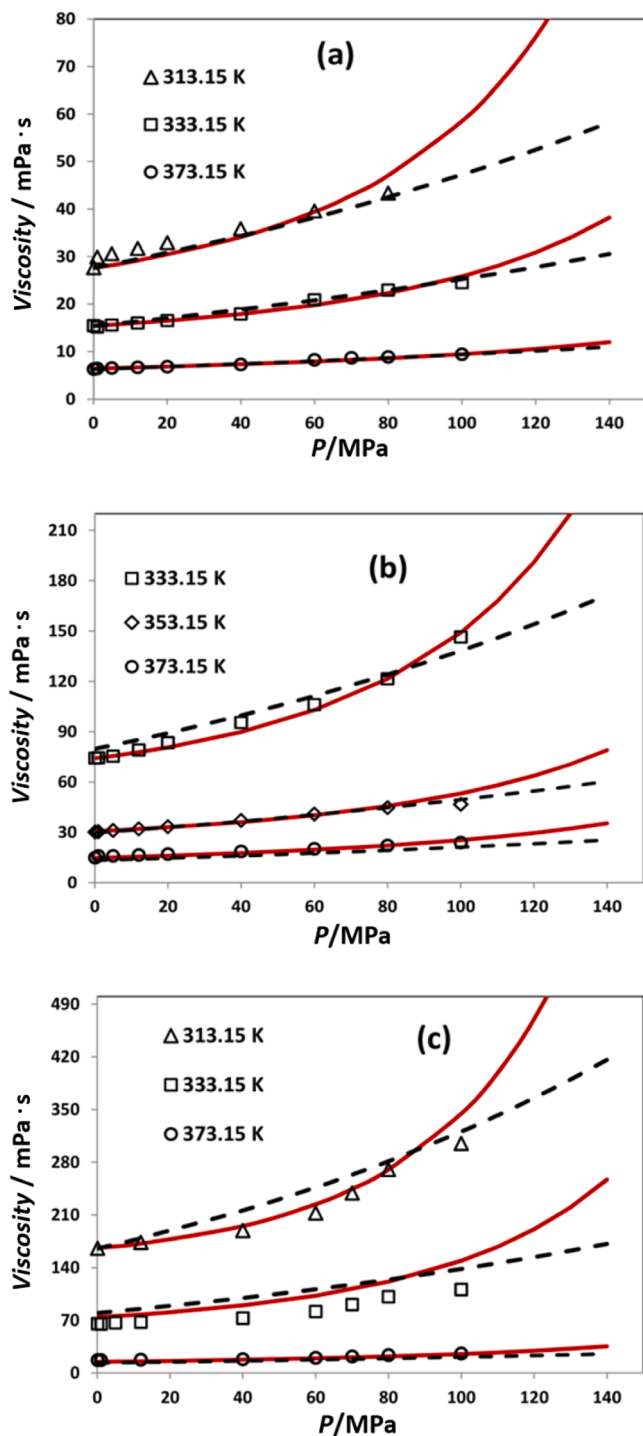


Fig. 3. Variation of viscosities for Ethaline (a), Reline (b), and Glyceline (c) at several isotherms. Unfilled symbols represent experimental viscosities from the literature [32], solid lines correspond to ERT-based model predictions, and dashed lines correspond to RHST-based model predictions.

of strong, directional hydrogen bonding. The peak positions and heights remain virtually unchanged with variations in temperature and pressure, indicating that the fundamental hydrogen-bonding geometry is preserved across all conditions, reflecting pronounced structural stability. The high peak intensity indicates substantial local ordering beyond that expected for random molecular packing, confirming that Cl⁻ acts as a structure-directing agent by organizing HBD molecules within its coordination sphere.

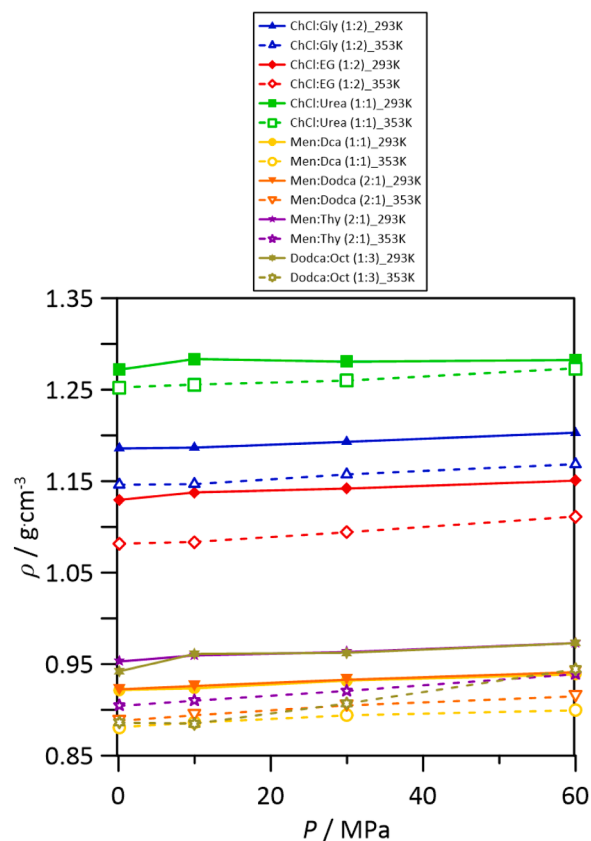


Fig. 4. MD-predicted densities of DESs systems under the considered conditions.

For menthol-based Type V DESs (panels d-f), Men(OH)⋯O(carbonyl) RDFs display broader peaks at slightly longer distances (2.2–2.5 Å) with lower intensities ($g(r)_{max} = 3-4$), indicating weaker and more flexible hydrogen bonding compared with the ion-dipole interactions in ChCl-based systems. The Dodca:Oct system (panel g) exhibits intermediate behavior, with peaks at 1.9–2.1 Å—surprisingly short distances that suggest particularly strong carboxylic acid dimer formation with partial proton sharing. The bimodal character observed in some RDFs, especially for the menthol-based systems, indicates the coexistence of multiple hydrogen bonding geometries, such as cyclic and linear dimers.

Homoassociation RDFs (Figs. 7–10) reveal that self-interactions persist even after DES formation. In ChCl-based systems, Ch-Cl ion pairing appears as peaks at 4.5–5.0 Å, while HBD-HBD interactions show characteristic hydrogen-bonding peaks at 2.4–2.8 Å. Remarkably, urea-urea homoassociations exhibit high intensities ($g(r)_{max} = 5-6$), approaching or even exceeding those of Cl-Urea heteroassociations. This self-association tendency of urea, arising from its dual donor-acceptor capability, explains Reline's unique properties and suggests that urea molecules form oligomeric clusters embedded within the ionic matrix—a bicontinuous nanostructure quite different from simple molecular mixing. In menthol-based DESs, menthol-menthol (Men-Men) homoassociations ($g(r)_{max} = 3-4$) substantially exceed fatty-acid self-associations ($g(r)_{max} = 1.8-2.5$), indicating preferential menthol clustering driven by both hydroxyl hydrogen bonding and hydrophobic interactions between cyclohexane rings.

Solvation numbers derived from RDF integration (Fig. 11) quantify coordination environments. In ChCl:Gly and choline chloride-ethylene glycol (ChCl:EG), Cl⁻ exhibits coordination numbers of $N = 4-5$ hydroxyl hydrogens, consistent with 1:2 stoichiometry and indicating that each Cl⁻ coordinates with 2–3 HBD molecules. Simultaneously, significant HBD-HBD coordination ($N = 2-3$) confirms competition between hetero- and homoassociations. ChCl:Urea displays comparable Cl-Urea

Table 6

Center of mass self-diffusion coefficients, D , of DESs systems calculated from MD simulations for the considered conditions.

DES system	Conditions	$10^{-11} D / \text{m}^2 \cdot \text{s}^{-1}$	
		HBA (Ch, Men, Oct)	HBD (Gly, EG, Urea, Dca, Dodca, Thy)
ChCl:Gly (1:2)	293 K, 0.1 MPa	0.908	0.909
	293 K, 10 MPa	0.941	0.940
	293 K, 30 MPa	1.213	1.211
	293 K, 60 MPa	0.946	0.947
	353 K, 0.1 MPa	3.134	3.136
	353 K, 10 MPa	3.468	3.450
	353 K, 30 MPa	4.502	4.504
	353 K, 60 MPa	3.973	3.972
	293 K, 0.1 MPa	0.945	0.946
	293 K, 10 MPa	1.799	1.800
ChCl:EG (1:2)	293 K, 10 MPa	1.465	1.466
	293 K, 30 MPa	1.326	1.328
	293 K, 60 MPa	6.804	6.803
	353 K, 0.1 MPa	3.975	3.973
	353 K, 10 MPa	4.790	4.793
	353 K, 30 MPa	4.387	4.385
	293 K, 0.1 MPa	1.189	1.197
	293 K, 10 MPa	1.529	1.532
	293 K, 30 MPa	1.495	1.498
	293 K, 60 MPa	1.543	1.558
ChCl:Urea (1:1)	353 K, 0.1 MPa	4.619	4.624
	353 K, 10 MPa	3.816	3.824
	353 K, 30 MPa	4.736	4.731
	353 K, 60 MPa	4.369	4.365
	293 K, 0.1 MPa	1.385	1.369
	293 K, 10 MPa	1.654	1.599
	293 K, 30 MPa	2.202	2.157
	293 K, 60 MPa	1.741	1.689
	353 K, 0.1 MPa	5.468	5.532
	353 K, 10 MPa	4.168	4.013
Men:Dca (1:1)	353 K, 30 MPa	4.930	5.056
	353 K, 60 MPa	5.539	5.412
	293 K, 0.1 MPa	1.049	1.021
	293 K, 10 MPa	1.377	1.333
	293 K, 30 MPa	1.842	1.878
Men:Dodca (2:1)			

Table 6 (continued)

DES system	Conditions	$10^{-11} D / \text{m}^2 \cdot \text{s}^{-1}$	
		HBA (Ch, Men, Oct)	HBD (Gly, EG, Urea, Dca, Dodca, Thy)
Men:Thy (2:1)	293 K, 60 MPa	1.440	1.497
	353 K, 0.1 MPa	4.945	4.883
	353 K, 10 MPa	3.928	3.998
	353 K, 30 MPa	4.557	4.497
	353 K, 60 MPa	4.819	4.887
	293 K, 0.1 MPa	1.621	1.599
	293 K, 10 MPa	1.933	1.904
	293 K, 30 MPa	2.601	2.593
	293 K, 60 MPa	2.072	2.097
	353 K, 0.1 MPa	6.547	6.577
Dodca:Oct (1:3)	353 K, 10 MPa	5.195	5.222
	353 K, 30 MPa	6.036	6.004
	353 K, 60 MPa	6.420	6.409
	293 K, 0.1 MPa	0.979	0.944
	293 K, 10 MPa	1.105	1.126
	293 K, 30 MPa	1.521	1.539
	293 K, 60 MPa	1.226	1.202
	353 K, 0.1 MPa	3.702	3.672
	353 K, 10 MPa	2.980	2.945
	353 K, 30 MPa	3.853	3.812
	353 K, 60 MPa	3.594	3.550

and Urea-Urea coordination numbers ($N = 3-4$ each), quantitatively confirming the pronounced urea self-association. Type V DESs show lower heteroassociation coordination ($N = 2-3$) alongside substantial Men-Men coordination, whereas Dodca:Oct exhibits higher homoassociation than heteroassociation—a distinctive feature suggesting that this system represents a borderline case between true DES behavior and conventional molecular mixture behavior.

Hydrogen bond populations (Fig. 12) were quantified using geometric criteria (distance $\leq 3.5 \text{ \AA}$, angle $\leq 30^\circ$). ChCl-based DESs exhibit $N_H(\text{Cl-HBD}) = 1.6-2.5$ hydrogen bonds per HBD molecule, with Cl-Urea showing the highest values. Homoassociation hydrogen bonds are also substantial: $N_H(\text{glycerol-glycerol, Gly-Gly}) = 1.2-1.5$, $N_H(\text{EG-EG}) = 1.4-1.8$, and remarkably, $N_H(\text{Urea-Urea}) = 1.8-2.2$, nearly matching heteroassociation levels. This indicates that approximately 40–50% of the total hydrogen bonds in Reline involve urea-urea interactions rather than the Cl-Urea interactions responsible for eutectic formation—a crucial insight for understanding this widely-studied DES. Type V DESs show lower hydrogen bond populations ($N_H = 0.5-1.2$), with near parity between hetero- and homoassociations, in contrast to the clear hetero-association dominance observed in Type III systems. Across all systems, hydrogen bond populations remain constant within $\pm 15\%$ under the investigated conditions, confirming the thermodynamic stability of the hydrogen-bonding networks.

Spatial distribution functions (SDFs, Figs. 13 and 14) visualize three-dimensional probability distributions of molecular arrangements. In

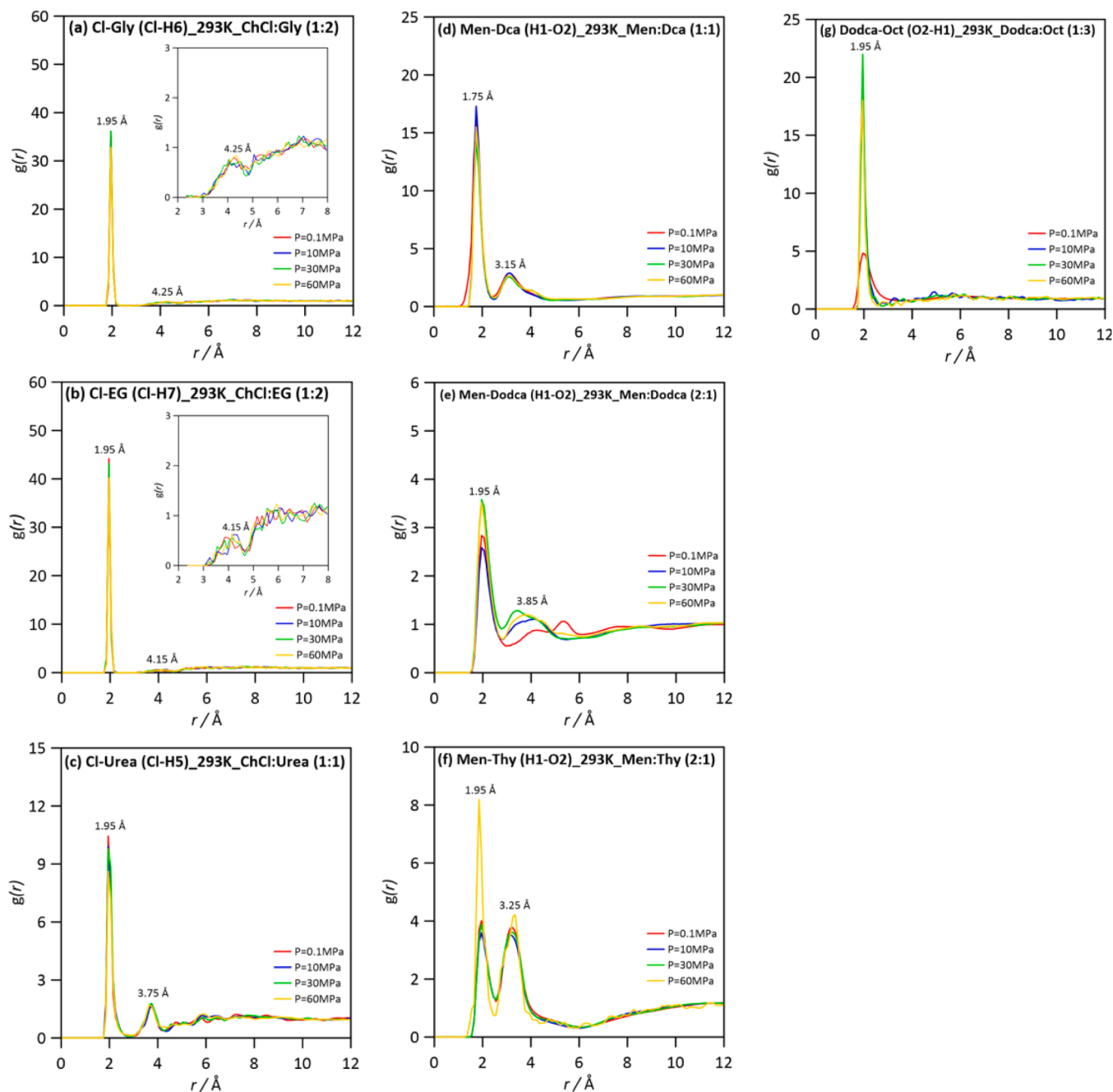


Fig. 5. Site-site Radial Distribution Functions, $g(r)$, for the reported HBA-HBD atomic pairs (atoms labelling as in Fig. 1) of the considered DESs systems at 293 K and 0.1, 10, 30 and 60 MPa.

ChCl-based DESs, four localized high-density lobes appear around choline with approximate tetrahedral symmetry, corresponding to preferred HBD positions for hydrogen bonding with adjacent Cl⁻ ions. These discrete, well-separated lobes indicate strong directional preferences. Type V DESs exhibit more diffuse distributions around menthol OH groups, reflecting greater angular flexibility. Increasing the temperature from 293 to 353 K causes slight lobe broadening without altering positions, whereas increasing pressure enhances lobe intensities without changing the spatial patterns—both observations confirming structural preservation across the investigated conditions.

Combined distribution functions (CDFs, Figs. 15 and 16) quantify hydrogen-bond geometries in distance-angle space. ChCl-based DESs and Dodca:Oct exhibit single, sharp maxima at ($r \approx 2.0$ – 2.2 Å, $\varphi \approx 0$ – 20°), characteristic of nearly linear hydrogen bonds with optimal

orbital overlap. Menthol-based DESs display bimodal angular distributions, with maxima at $\varphi \approx 10$ – 30° and $\varphi \approx 50$ – 80° , indicating the coexistence of linear and bent hydrogen-bonding configurations. This geometric versatility may contribute to the lower melting points and higher fluidity observed in Type V DESs. The CDF patterns remain unchanged across the investigated conditions, with only minor distance compressions ($\Delta r \approx 0.05$ Å) at 60 MPa.

Intermolecular interaction energies (Fig. 17) quantify the strengths of molecular interactions. In ChCl-based DESs, Ch-Cl interactions exhibit $E_{\text{inter}} = -250$ to -200 kJ·mol⁻¹, dominated by Coulombic interactions; Cl-HBD heteroassociations show $E_{\text{inter}} = -90$ to -55 kJ·mol⁻¹; and HBD-HBD homoassociations range from $E_{\text{inter}} = -50$ to -20 kJ·mol⁻¹. Notably, Urea-Urea interactions ($E_{\text{inter}} = -50$ to -40 kJ·mol⁻¹) are approximately 1.5 times stronger than Gly-Gly or EG-EG interactions,

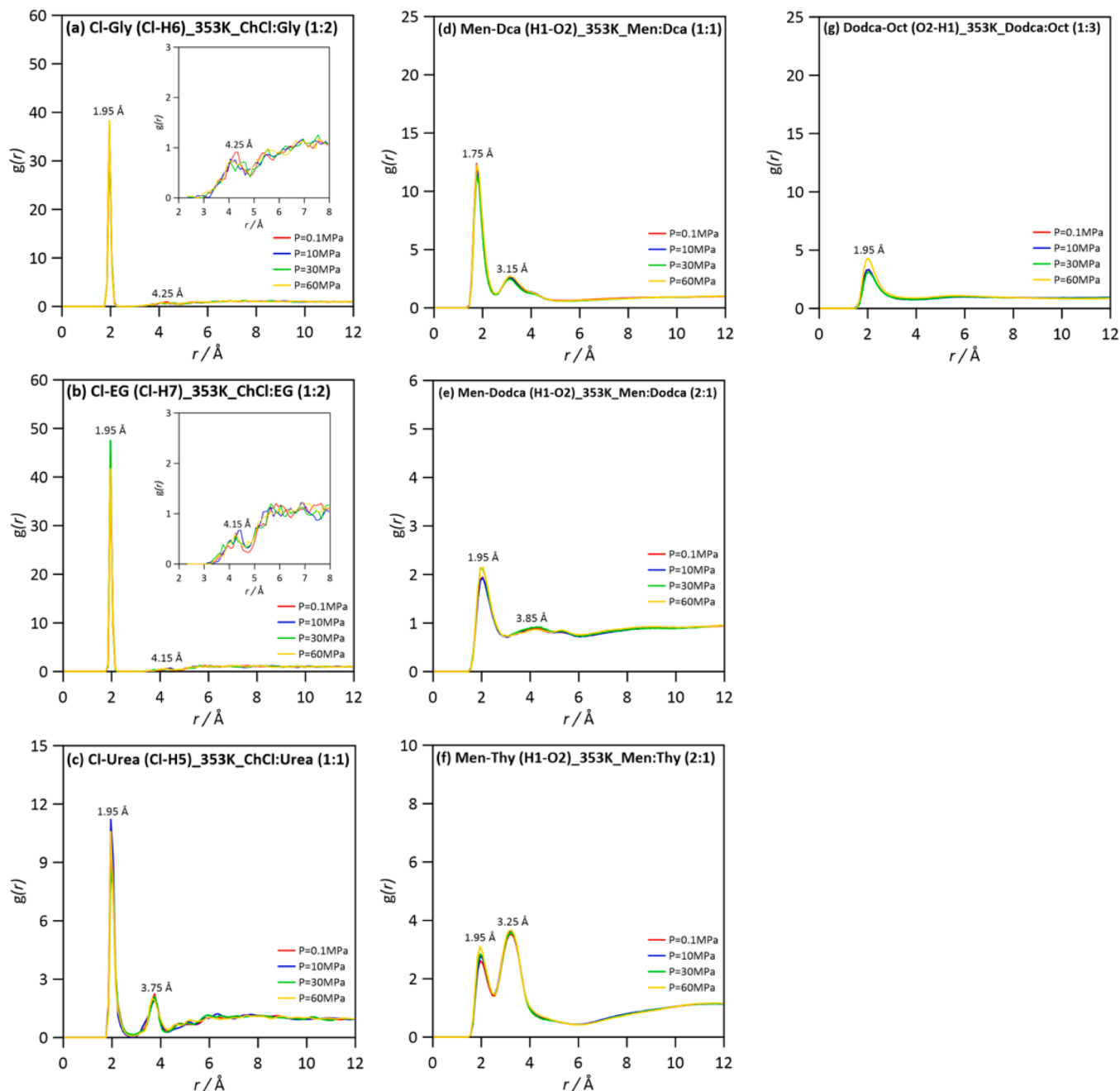


Fig. 6. Site-site Radial Distribution Functions, $g(r)$, for the reported HBA-HBD atomic pairs (atoms labelling as in Fig. 1) of the considered DESs systems at 353 K and 0.1, 10, 30 and 60 MPa.

quantitatively explaining urea's pronounced self-association. Type V DESs exhibit weaker interactions: Men-HBD heteroassociations range from $E_{inter} = -50$ to -30 kJ·mol⁻¹, and homoassociations range from $E_{inter} = -25$ to -10 kJ·mol⁻¹. The heteroassociation-to-homoassociation energy ratio is approximately 2.5:1 for ChCl systems, but only 1.5–2.0:1 for Type V systems, confirming a weaker thermodynamic driving force for eutectic formation in neutral DESs. Dodca:Oct shows nearly equivalent homo- and heteroassociation energies ($E_{inter} = -25$ to -15 kJ·mol⁻¹), consistent with its borderline DES character. Remarkably, all interaction energies remain constant within $\pm 10\%$ across the investigated conditions, confirming that these thermodynamic driving forces are intrinsic molecular properties rather than condition-dependent phenomena.

Overall, the results reveal a strong correspondence between the

macroscopic properties and molecular-level features of DESs. The semi-empirical models successfully capture the pressure- and temperature-dependent behavior of density, compressibility, and viscosity, while molecular dynamics simulations provide structural justification for these trends. The persistence of hydrogen-bond networks and the formation of locally ordered domains observed in MD trajectories explain the relatively low compressibility and the non-linear viscosity behavior at high pressures. Similarly, the interplay between hydrogen-bond strength and hydrophobic alkyl-chain interactions governs the deviations observed across different DES compositions. This agreement between model predictions and atomistic observations demonstrates that the macroscopic response of DESs under compression arises directly from their microscopic organization and interaction landscape.

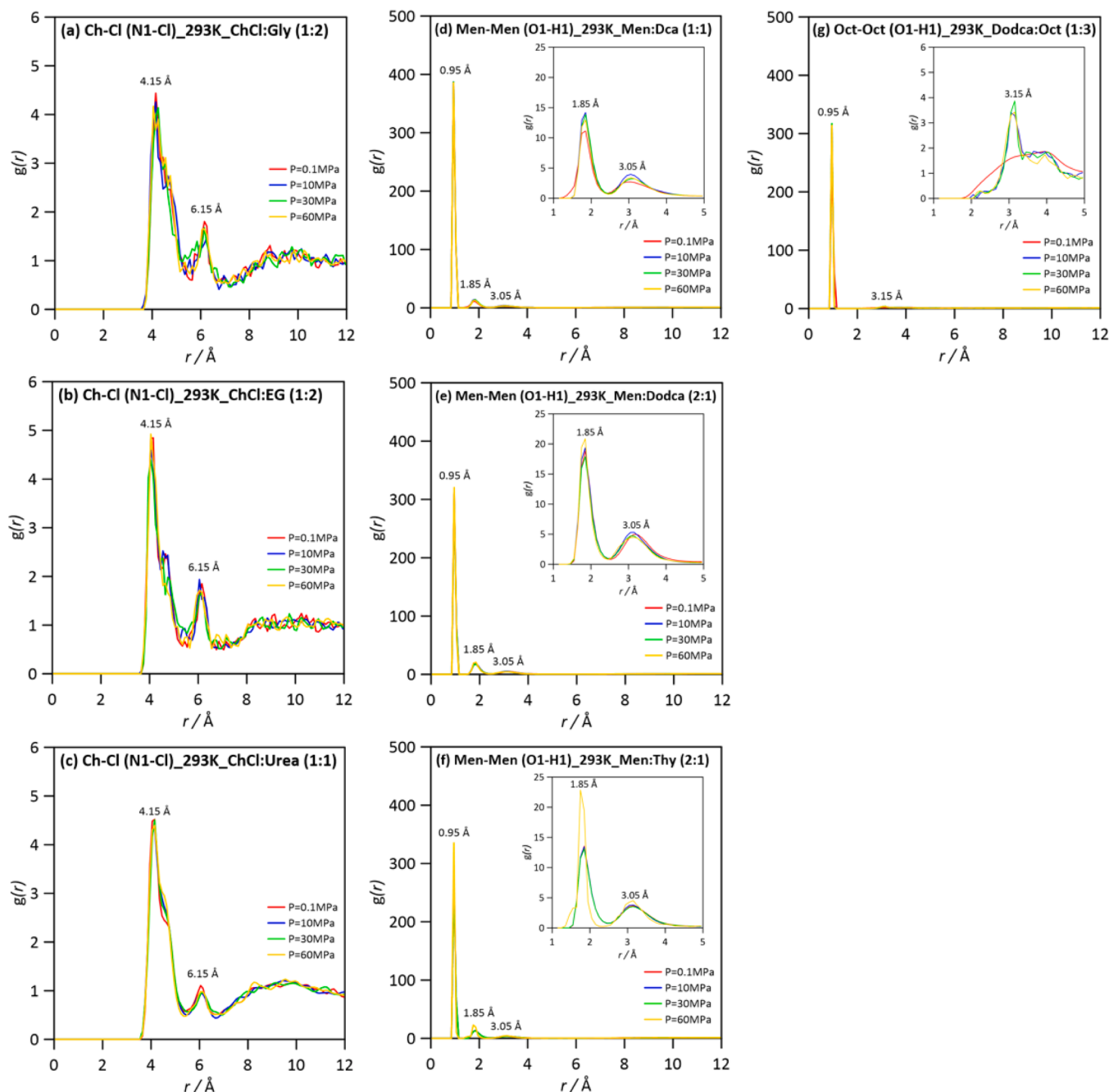


Fig. 7. Site-site Radial Distribution Functions, $g(r)$, for the reported HBA-HBA atomic pairs (atoms labelling as in Fig. 1) of the considered DESs systems at 293 K and 0.1, 10, 30 and 60 MPa.

3.4. Semiempirical modelling of CO₂ solubility

High-pressure CO₂ solubilities in three representative DESs—Reline, Glyceline, and Ethaline—were analyzed and correlated using the revised μ - μ approach combined with the PHS EoS. The correlations were performed at several isotherms by introducing an adjustable binary interaction parameter (k_{ij}) within the cross-energy term to account for specific solute–solvent interactions. The results are summarized in Table 7, where the AARDs of the calculated CO₂ solubilities (expressed as mole fractions) are compared with experimental data reported in the literature [74–76].

The combined PHS EoS + μ - μ model successfully reproduced 115 experimental data points for CO₂ solubility in the selected DESs over the temperature range 303.15–343.15 K and pressures up to 6347 MPa,

achieving an overall AARD of 9.95%. This level of agreement indicates that the proposed semi-empirical framework provides a reliable description of gas solubility behavior in complex, hydrogen-bonded solvent systems, particularly under moderate pressures. The ability of the model to capture solubility trends with minimal parameter adjustment confirms that the essential thermodynamic features—molecular packing, interaction energy, and the non-ideal nature of gas–liquid mixing—are adequately represented within the PHS-based formalism.

As expected, the solubility of CO₂ increased with pressure and decreased with temperature for all three DESs studied, consistent with Henry's law behavior and the exothermic nature of CO₂ dissolution in polar liquids. The decrease in solubility with temperature arises from the weakening of CO₂–solvent interactions as thermal motion disrupts hydrogen bonding and reduces the solvent's ability to stabilize dissolved

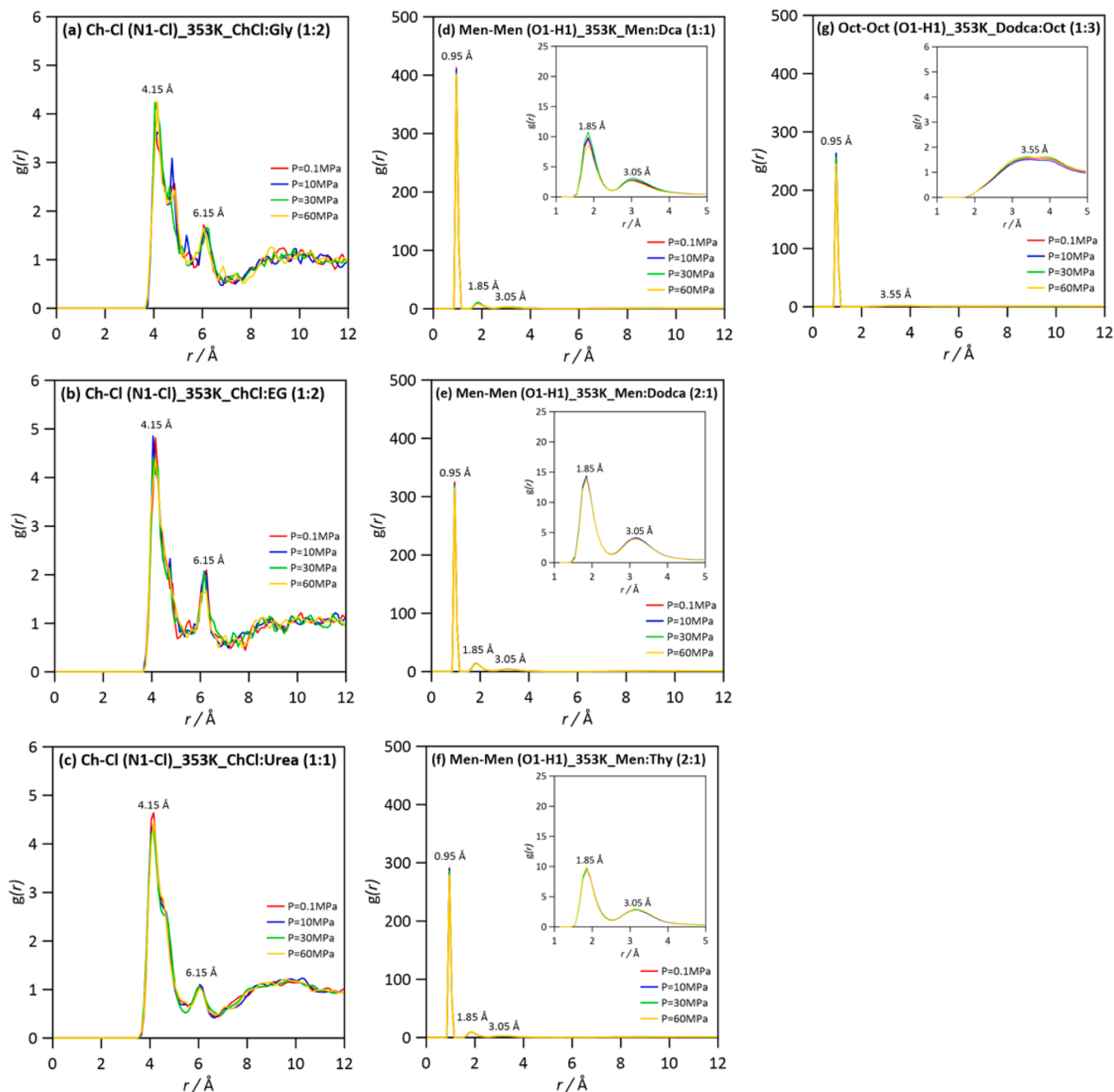


Fig. 8. Site-site Radial Distribution Functions, $g(r)$, for the reported HBA-HBA atomic pairs (atoms labelling as in Fig. 1) of the considered DESs systems at 353 K and 0.1, 10, 30 and 60 MPa.

gas molecules. This trend is well captured by the μ - μ approach through the temperature-dependent behavior of the k_{ij} parameter, which modulates the effective interaction energy between CO₂ and the DES components.

The fitted k_{ij} values exhibited different temperature dependencies among the three systems. For CO₂ in Ethaline, k_{ij} decreased with increasing temperature, indicating a progressive reduction in the effective attraction between CO₂ and the solvent mixture, consistent with the observed decrease in solubility at higher temperatures. In contrast, the behavior of k_{ij} for CO₂ in Reline and Glyceline did not follow a consistent trend: the parameter increased at some isotherms and decreased at others. Such irregular variations likely reflect the complex interplay between the hydrogen-bonding network, solvent polarity, and CO₂-solute association dynamics in these multicomponent

systems. Local structural rearrangements and the different affinities of HBD and HBA sites toward CO₂ likely cause the non-monotonic temperature dependence of k_{ij} .

Despite these variations, a general qualitative relationship can be observed between the magnitude of k_{ij} and the overall CO₂ affinity of each DES. Systems with higher k_{ij} values—corresponding to weaker cross-interactions—tend to exhibit lower CO₂ solubilities, whereas smaller k_{ij} values indicate stronger solute-solvent interactions and enhanced gas uptake. This relationship underscores the physical meaning of k_{ij} as a measure of interaction strength within the semi-empirical μ - μ framework.

Hence, the PHS EoS combined with the revised μ - μ approach provides a simple yet physically meaningful method to correlate and predict CO₂ solubility in DESs over moderate temperature and pressure ranges.

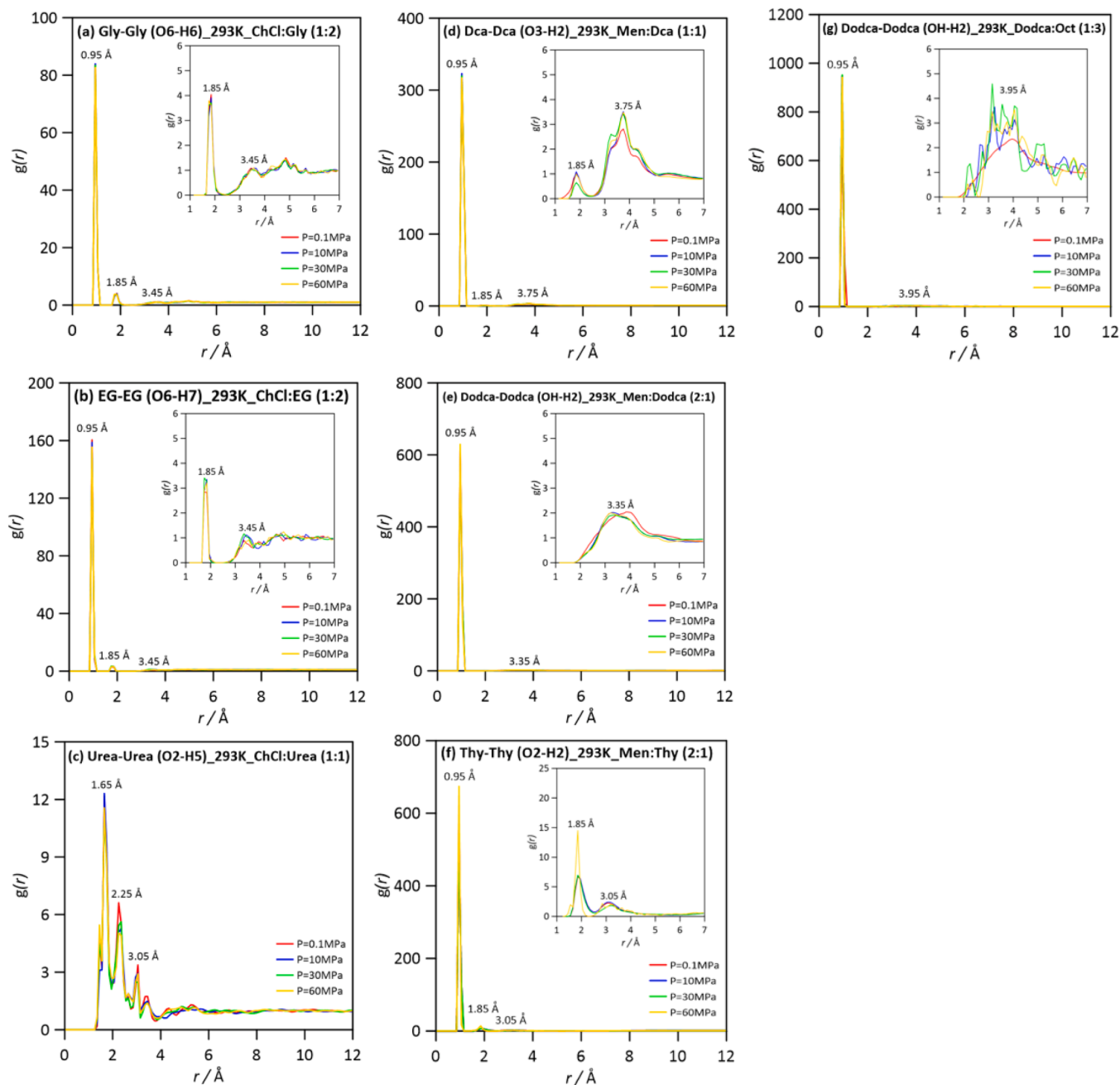


Fig. 9. Site-site Radial Distribution Functions, $g(r)$, for the reported HBD-HBD atomic pairs (atoms labelling as in Fig. 1) of the considered DESs systems at 293 K and 0.1, 10, 30 and 60 MPa.

The results confirm that solubility is primarily governed by pressure, temperature, and the strength of CO₂-solvent interactions represented by the k_{ij} parameter. While the current model captures the main experimental trends with reasonable accuracy, incorporating an explicit temperature dependence of k_{ij} could further improve predictive performance. Such refinement would allow the model to describe more accurately the competing effects of hydrogen bonding, molecular polarity, and free-volume changes that control gas solubility in DESs under varying thermodynamic conditions.

The variation of the k_{ij} parameter across temperature and solvent composition reflects the strength and specificity of CO₂-DES interactions. Lower k_{ij} values correspond to stronger attractive forces between CO₂ and the solvent, resulting in higher solubilities. In the case of Ethaline, the systematic decrease in k_{ij} with increasing temperature indicates a weakening of these interactions as thermal agitation disrupts

hydrogen-bonded solvation shells. Conversely, the less regular temperature dependence observed for Reline and Glyceline arises from the coexistence of competing interactions—hydrogen bonding between urea or glycerol sites and CO₂ on one hand, and dispersion interactions from the choline cation and alkyl chains on the other. This complex interplay produces non-monotonic behavior of k_{ij} , consistent with the mixed physical-chemical absorption mechanism.

Thus, the fitted k_{ij} values not only reproduce experimental solubilities but also serve as quantitative indicators of solute-solvent affinity and the balance between polar and dispersive contributions to CO₂ stabilization. These results collectively demonstrate that the macroscopic thermophysical trends modeled semi-empirically directly reflect molecular-scale organization and hydrogen-bonding motifs which are further analyzed in the following section via MD simulations.

It should be noted that the present PHS EoS + μ - μ formulation is

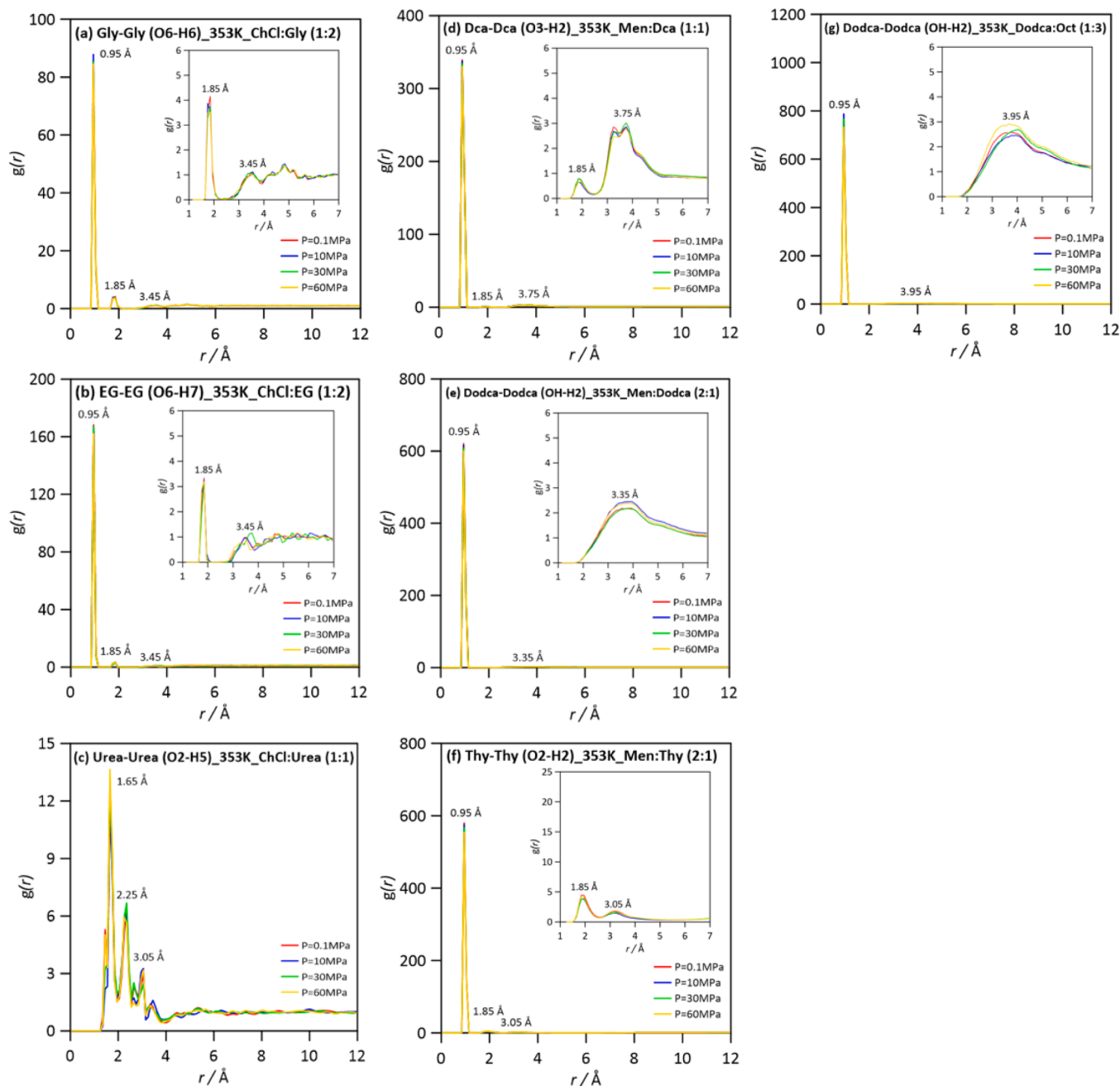


Fig. 10. Site-site Radial Distribution Functions, $g(r)$, for the reported HBD-HBD atomic pairs (atoms labelling as in Fig. 1) of the considered DESs systems at 353 K and 0.1, 10, 30 and 60 MPa.

limited to pure or early pure DES systems. In the presence of water or other impurities, the hydrogen-bond network and local polarity can change substantially, which may require re-parameterization of the model or the introduction of additional composition-dependent terms and then implies the limitation of model's applicability under the practical applications involving the moisture or impurities.

3.5. MD modelling of CO₂ solubility

To elucidate the molecular mechanisms underlying CO₂ capture, interfacial MD simulations were performed for ChCl:Gly, ChCl:EG, and ChCl:Urea in contact with pure CO₂ at 303 and 343 K and pressures from 10 to 60 MPa. Figs. 18 and 19 present number density profiles perpendicular to the DES-CO₂ interface, revealing the spatial distribution of molecular species across the interfacial region. The profiles exhibit three

distinct zones: (1) a pure CO₂ gas-like region at large distances from the interface, characterized by constant CO₂ density and negligible DES component density; (2) a sharp interfacial transition region spanning approximately 10–15 Å where CO₂ density increases dramatically as gas molecules encounter the liquid surface while DES component densities begin to rise; and (3) a bulk DES liquid region, where CO₂ is dissolved and uniformly distributed, and DES components reach their bulk liquid densities.

The interfacial profiles demonstrate efficient CO₂ transfer through a three-stage mechanism: (1) diffusion through the external CO₂ phase toward the interface, driven by concentration gradients; (2) adsorption at the interface, where CO₂ molecules accumulate in a compressed layer, evidenced by a density enhancement ($\sim 1.5\text{--}2.0 \times$ bulk gas density) immediately adjacent to the DES surface; and (3) rapid penetration into the bulk liquid phase, with CO₂ density equilibrating within 10–15 Å of

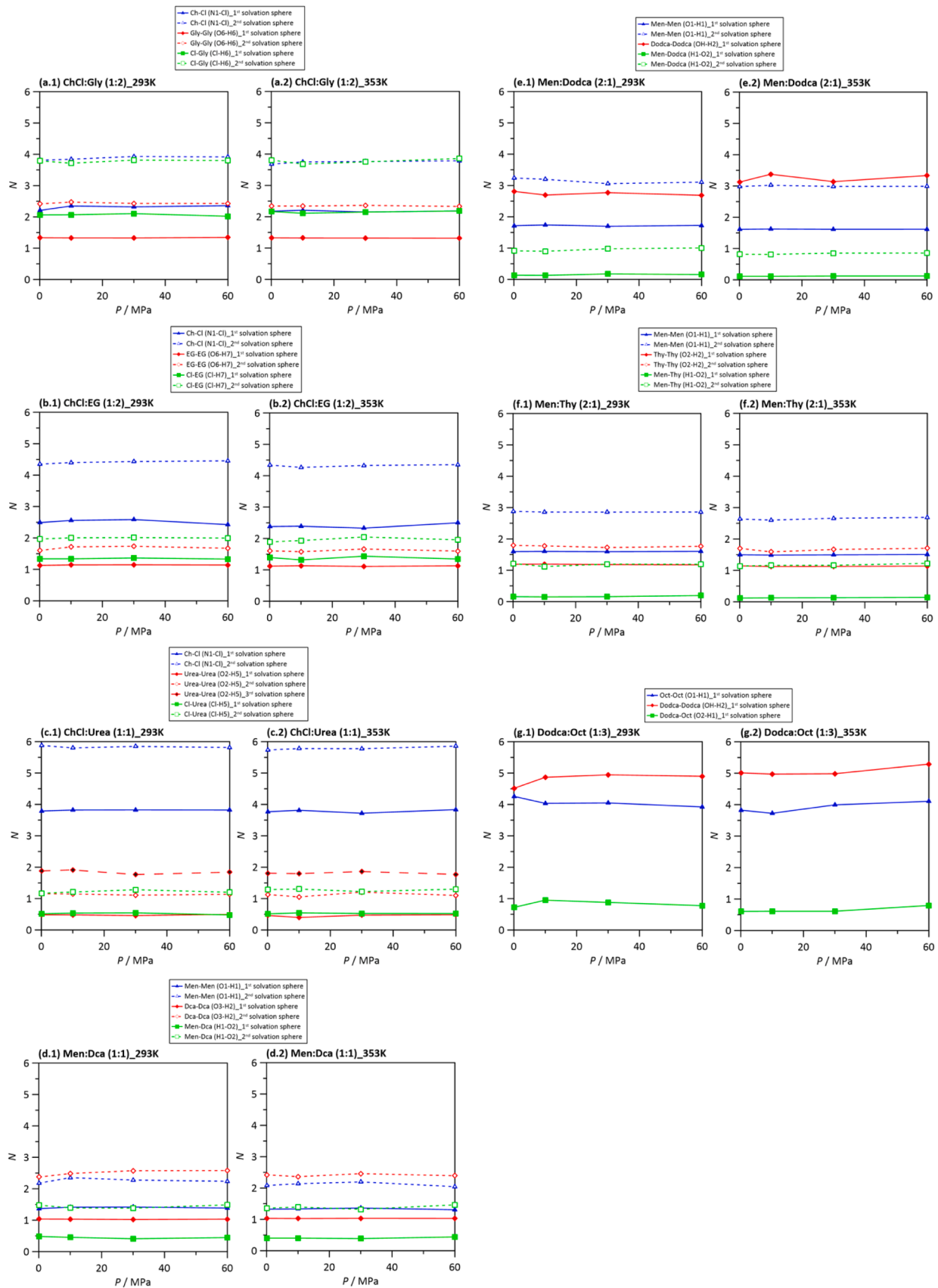


Fig. 11. Solvation numbers, N , obtained from the integration of Radial Distribution Functions reported in Figs. 5–10, corresponding to the first, second and/or third solvation shells, defined by the first, second and/or third minima in the corresponding Radial Distribution Function for the considered DESs systems under the reported conditions. Atom labelling is as in Fig. 1.

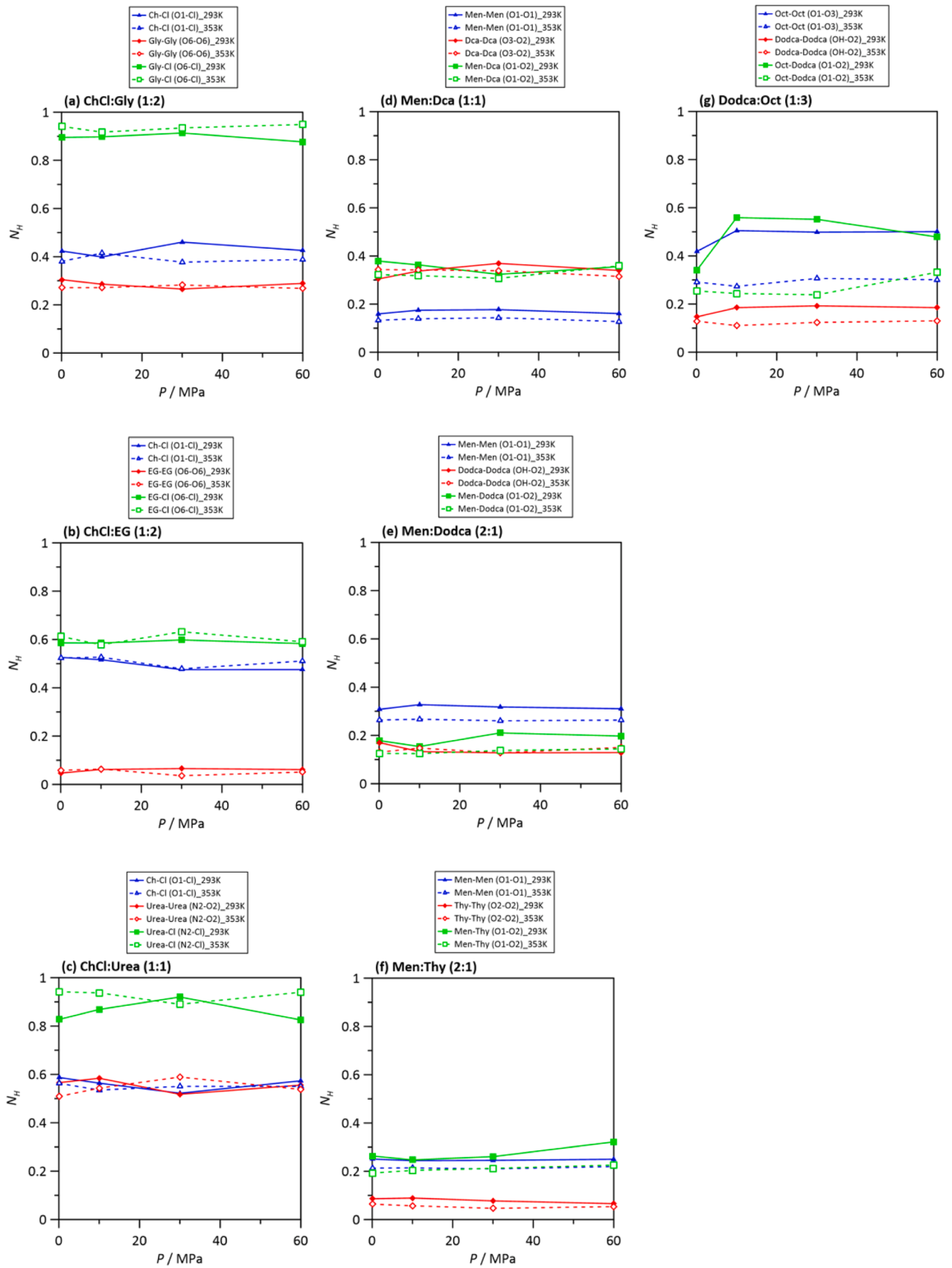


Fig. 12. Average number of hydrogen bonds per HBD molecule, N_H , for the reported atomic pairs in the considered DESs systems under the selected conditions. Atom labelling is as in Fig. 1.

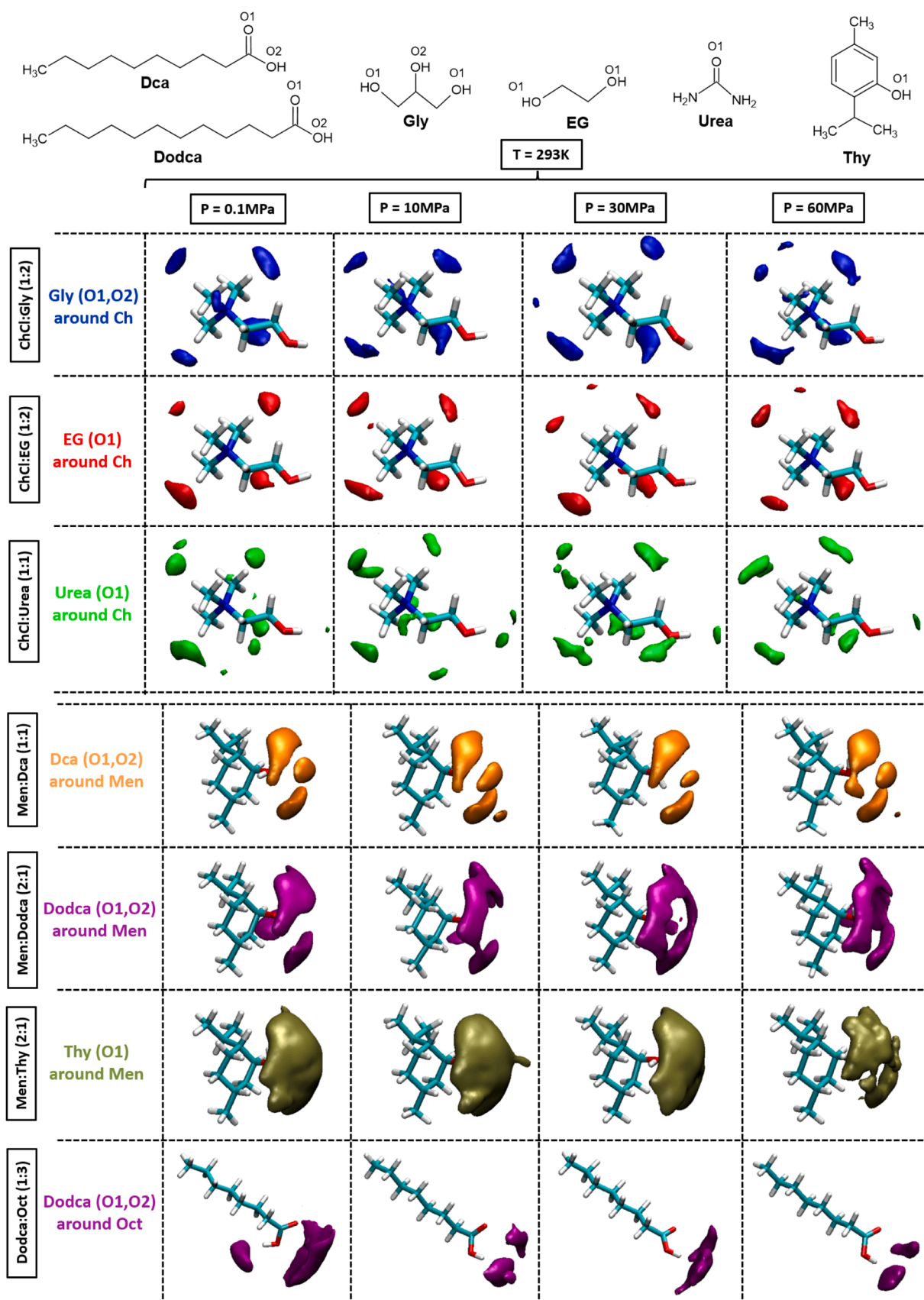


Fig. 13. Spatial Distribution Functions, SDFs, for the reported atomic pairs of the considered DESs systems at 293 K and 0.1, 10, 30 and 60 MPa.

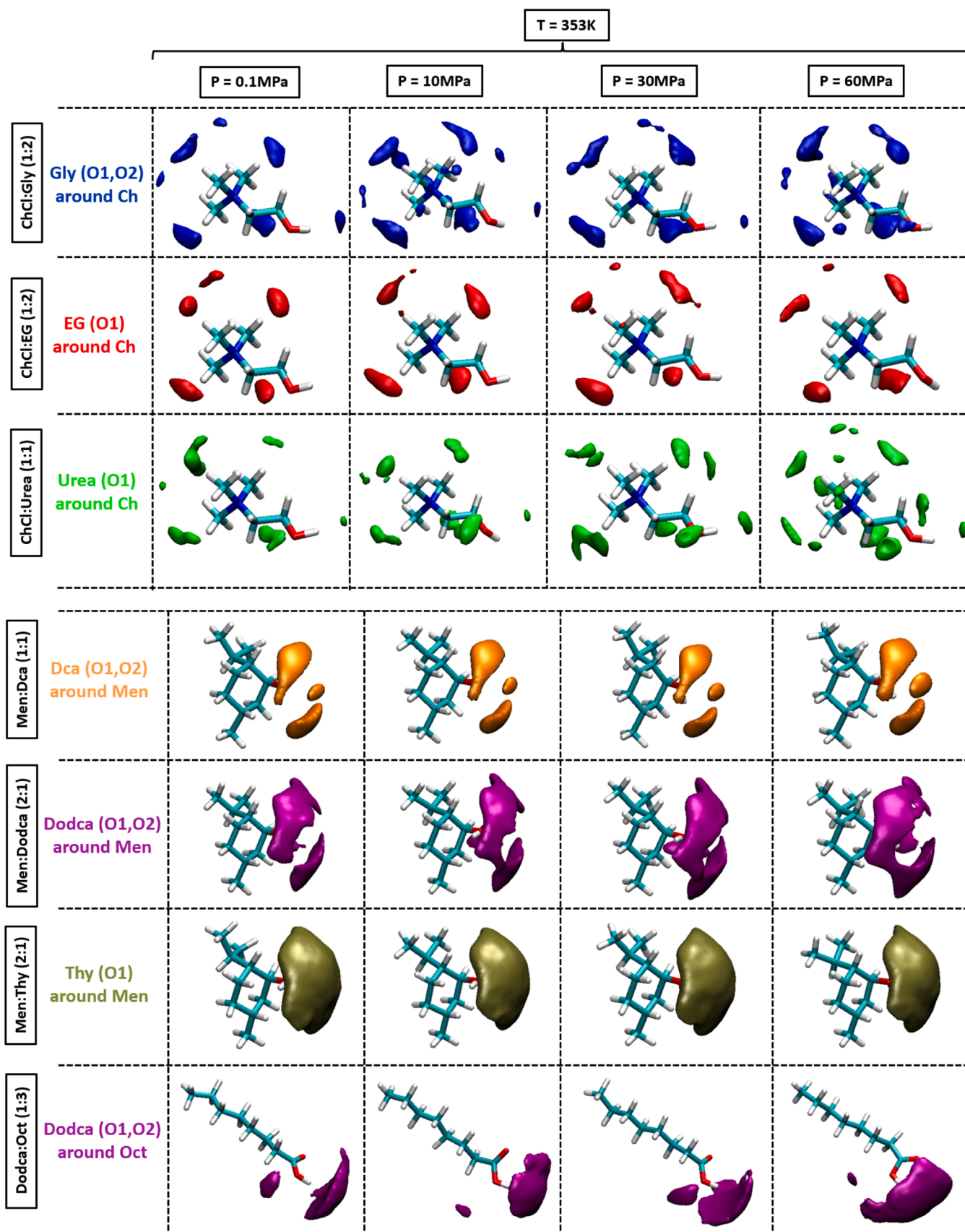


Fig. 14. Spatial Distribution Functions, SDFs, for the reported atomic pairs (atoms labelling as in Fig. 13) of the considered DESs systems at 353 K and 0.1, 10, 30 and 60 MPa.

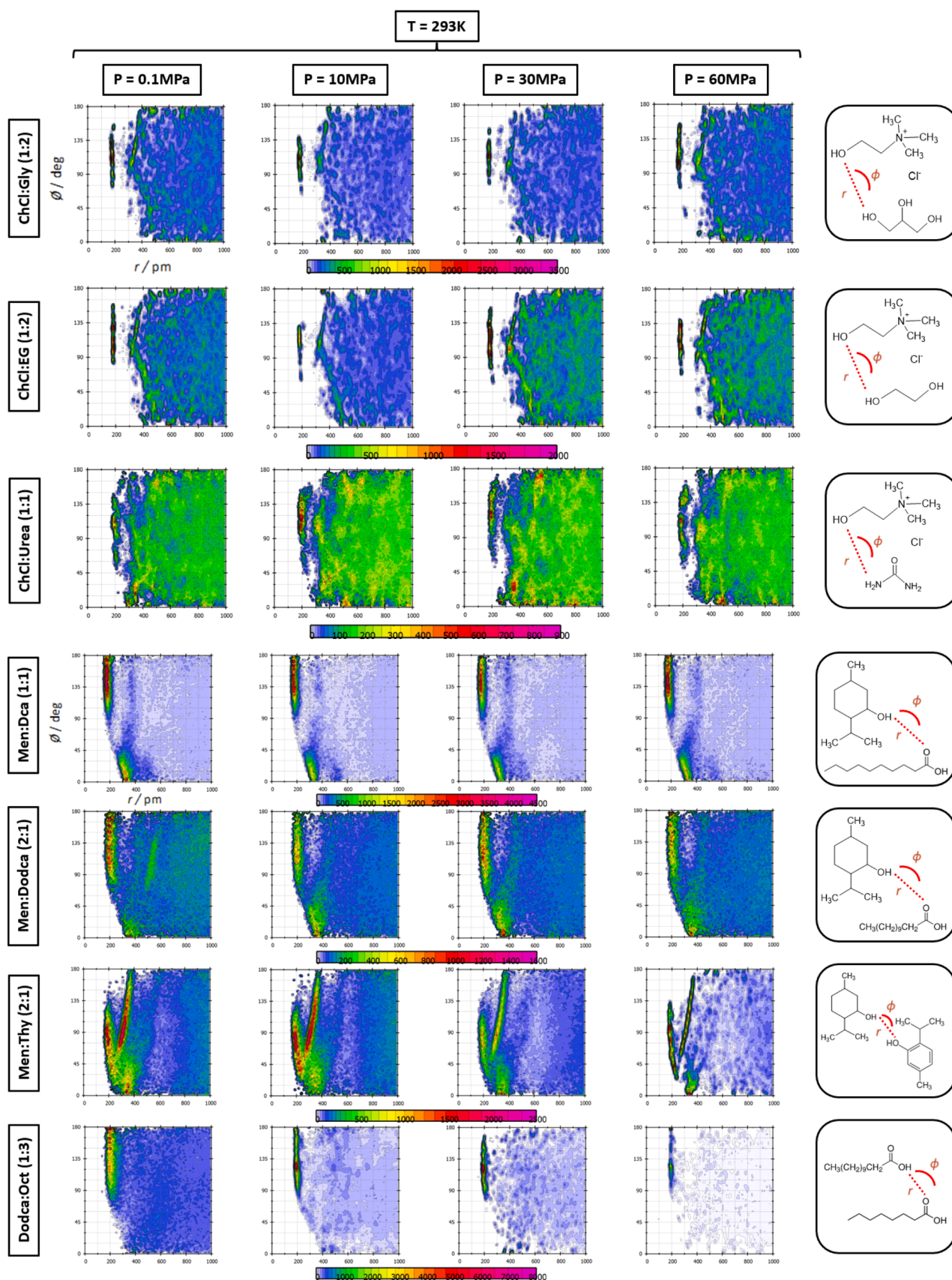


Fig. 15. Combined Distribution Functions, CDFs, for the reported distances, r , and angles, ϕ , of HBA-HBD interactions in the considered DESs systems at 293 K and 0.1, 10, 30 and 60 MPa.

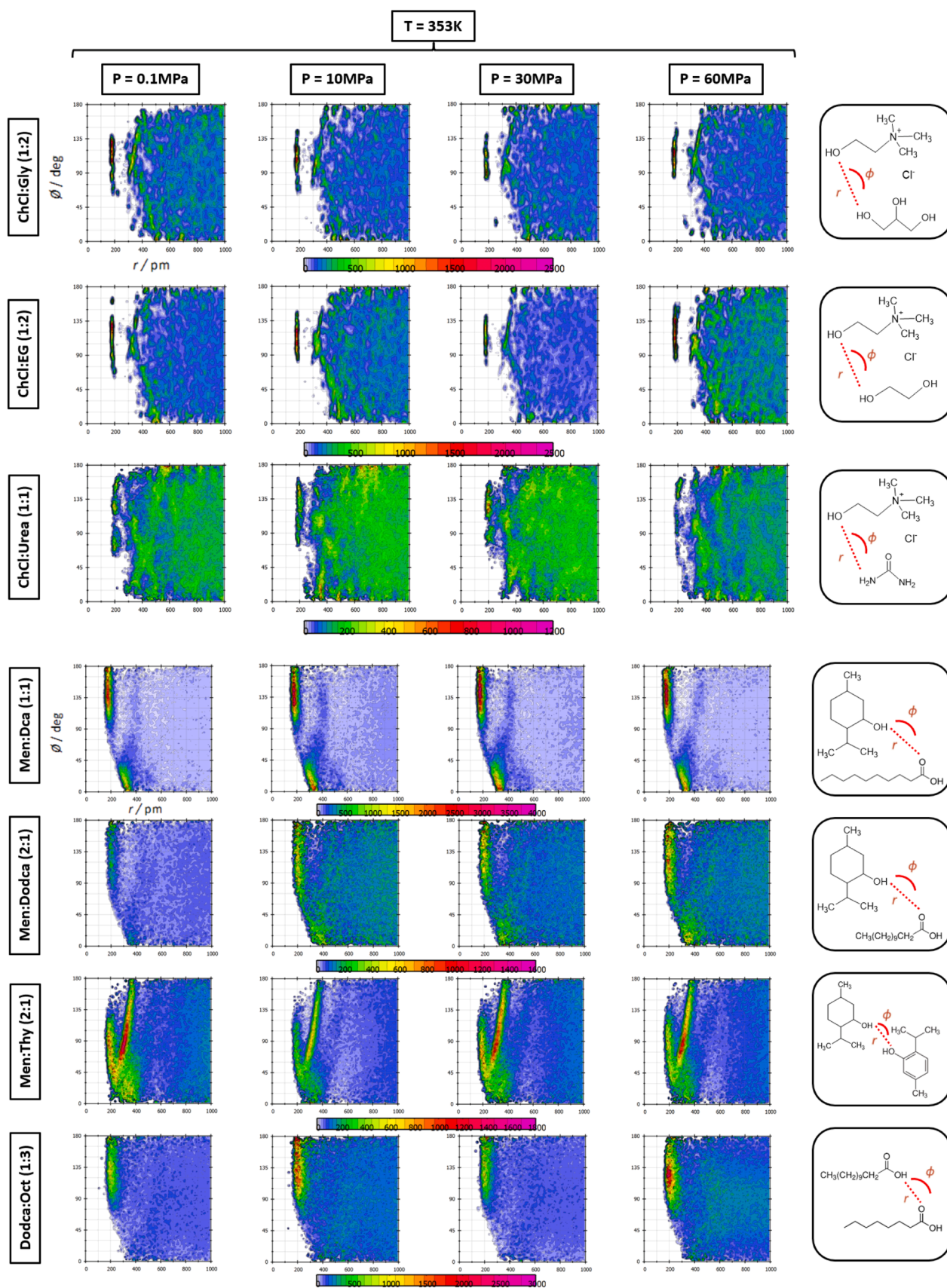


Fig. 16. Combined Distribution Functions, CDFs, for the reported distances, r , and angles, ϕ , of HBA-HBD interactions in the considered DESs systems at 353 K and 0.1, 10, 30 and 60 MPa.

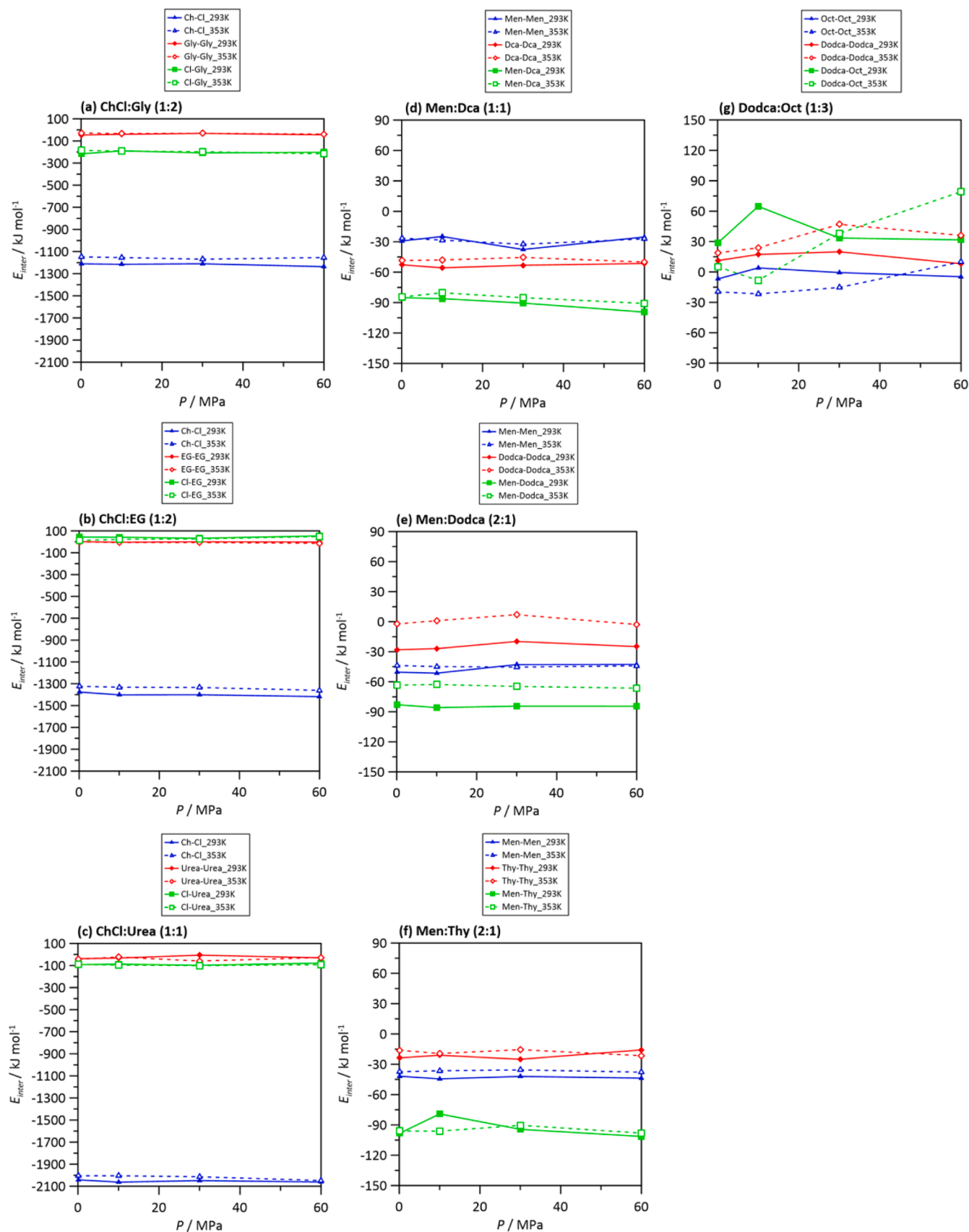


Fig. 17. MD intermolecular interaction energies (sum of Lennard-Jones and coulombic contributions) for DESs systems under the considered conditions.

Table 7

AARDs of correlated high-pressure CO₂ solubility for selected DESs using the PHS EoS (Eq. 1) combined with the μ - μ approach, including the revision factor (Eq. 18) and binary interaction parameters, k_{ij} , obtained from experimental measurements.

DES	Δx_{CO_2}	$\Delta P(\text{MPa})$	$T(\text{K})$	NP	AARD	k_{ij}	AARD	Data Source
Glyceline	0.0026–0.0623	0.187–5.873	303.15	8	9.70	1.3412	> 100	[74]
	0.002–0.0524	0.191–5.991	313.15	8	10.03	1.3420	> 100	
	0.0016–0.0455	0.196–6.17	323.15	8	10.73	1.3443	> 100	
	0.0013–0.0368	0.201–6.265	333.15	8	10.90	1.3419	> 100	
	0.001–0.0280	0.203–6.347	343.15	8	10.06	1.3348	> 100	
Reline	0.0050–0.0621	0.299–5.654	303.15	7	6.75	1.0888	> 100	[75]
	0.00483–0.0531	0.350–5.722	313.15	7	6.94	1.0873	> 100	
	0.00407–0.0478	0.356–5.782	323.15	7	7.35	1.0868	> 100	
	0.00345–0.0413	0.362–5.845	333.15	7	7.70	1.0912	> 100	
	0.00280–0.0345	0.371–5.911	343.15	7	7.92	1.0925	> 100	
Ethaline	0.0019–0.0533	0.236–5.863	303.15	8	13.45	1.1188	> 100	[76]
	0.0016–0.0499	0.248–5.902	313.15	8	13.11	1.1129	> 100	
	0.0016–0.0379	0.306–6.167	323.15	8	12.35	1.1086	> 100	
	0.0014–0.0277	0.332–6.104	333.15	8	11.20	1.1027	> 100	
	0.0013–0.0214	0.378–6.323	343.15	8	9.72	1.0939	> 100	
Overall					115	9.95		> 100

initial contact. The absence of significant CO₂ accumulation or density oscillations beyond the immediate interfacial zone indicates facile dissolution without the formation of persistent interfacial barriers—a favorable characteristic for mass transfer-limited capture processes.

Temperature effects are inferred from the density profiles: at 343 K, the interfacial region broadens slightly, and CO₂ penetration depth increases compared to 303 K, consistent with enhanced molecular mobility and reduced hydrogen-bond network rigidity at elevated temperature. However, the fundamental three-stage mechanism remains unchanged, and CO₂ ultimately achieves uniform distribution throughout the DES liquid phase regardless of temperature. Pressure effects are primarily reflected in increased CO₂ density in both gas and liquid phases, with minimal impact on interfacial structure or transfer mechanism. At 60 MPa, CO₂ densities in the adsorbed interfacial layer approach those of liquid CO₂, yet efficient penetration into the DES phase continues.

Comparison among the three DESs reveals subtle differences: ChCl:Urea shows the sharpest interfacial transition (narrowest interfacial width, ~ 10 Å), likely due to its more structured bulk liquid arising from strong urea-urea associations, whereas ChCl:Gly exhibits a somewhat broader interface (~ 15 Å), potentially reflecting glycerol's conformational flexibility and a more heterogeneous surface. ChCl:EG displays intermediate behavior. Despite these minor variations, all three systems demonstrate rapid and efficient CO₂ transfer from the gas to the liquid phase, supporting their viability for practical CO₂ capture applications.

To further quantify these differences at the molecular level, and to establish a more quantitative connection between molecular simulations and thermodynamic modeling, the CO₂-DESs interaction energies obtained from MD simulations were analyzed (Fig. 20). A clear correlation is observed between the magnitude of the interaction energy and the CO₂ solubility trends as well as the binary interaction parameter (k_{ij}) in Table 7. Although the k_{ij} parameter is empirical and not directly derived from MD simulations, its variation can be consistently interpreted in light of these molecular-level descriptors. Systems exhibiting more negative interaction energies (i.e., stronger DES-CO₂ attractive interactions), such as ChCl:Urea (Ch-CO₂), correspond to enhanced CO₂ affinity and lower effective k_{ij} values. In contrast, weaker interaction energies, as observed for ChCl:EG (Ch-CO₂), are consistent with reduced CO₂ affinity and higher k_{ij} values. Additionally, the pressure dependence of interaction energy shows systematic trends that mirror changes in CO₂ solubility, with stronger interactions generally observed at higher pressures, reflecting increased CO₂ density and enhanced contact with the DES phase. Temperature effects are also consistent, with weaker (less negative) interaction energies at higher temperature, in agreement with the experimentally observed decrease in CO₂ solubility. Therefore, these results demonstrate that the interaction energy obtained from MD

simulations provides a physically meaningful and quantitative descriptor that directly relates to macroscopic thermodynamic parameters, thereby reinforcing the connection between molecular simulations and the semi-empirical model.

Despite the detailed structural and interfacial insights obtained from MD simulations, it is important to note that no explicit free-energy calculations (e.g., solvation free energies or excess chemical potentials) were performed in the present work. From a rigorous thermodynamic perspective, CO₂ solubility is governed by the excess chemical potential (ΔG_{solv}) of the solute in the solvent phase. In principle, this quantity can be computed from molecular simulations using methods such as Widom Test-Particle Insertion (TPI) [77], Thermodynamic Integration (TI) [78], Free-Energy Perturbation (FEP) [79], or Bennett Acceptance Ratio (BAR) [80]. For example, the excess chemical potential (μ_{ex}) can be expressed as [77]:

$$\mu_{ex} = -k_B T * \ln \left\langle \frac{1}{V} \int ds_{N+1} \exp(-\beta \Delta U) \right\rangle_N \quad (27)$$

Here, $\beta = 1/k_B T$, k_B is the Boltzmann constant, V and T are the system volume and temperature, respectively, and $\Delta U \equiv U(s^{N+1}) - U(s^N)$ is the energy difference for systems with N and $N + 1$ particles. From μ_{ex} , Henry's constant and solubility can be directly derived. However, the application of these methods to DESs is computationally challenging due to their high density, strong hydrogen-bonding networks, and slow structural relaxation, which significantly hinder statistical convergence—particularly for PI techniques. More robust approaches such as TI require extensive sampling over multiple coupling states, typically increasing the computational cost by an order of magnitude compared with standard MD simulations.

In this work, the semi-empirical and molecular dynamics components are intentionally treated as complementary but independent frameworks. The former, calibrated against experimental thermodynamic data, captures the macroscopic behavior of the system, while MD simulations provide mechanistic and molecular-level insight into CO₂ solvation. Their agreement supports the physical consistency of the results, although MD simulations are not used as direct parameter sources for the PHS or μ - μ models. Instead, they enable the interpretation of the effective interactions embedded in the model parameters. In particular, the trends observed in intermolecular interaction energies are consistent with the magnitude and temperature dependence of the binary interaction parameter (k_{ij}), providing an indirect but physically meaningful connection between molecular structure and macroscopic solubility. Nevertheless, the explicit calculation of ΔG_{solv} and related quantities represents an important direction for future work, which would enable a fully quantitative link between molecular simulation and thermodynamic modeling.

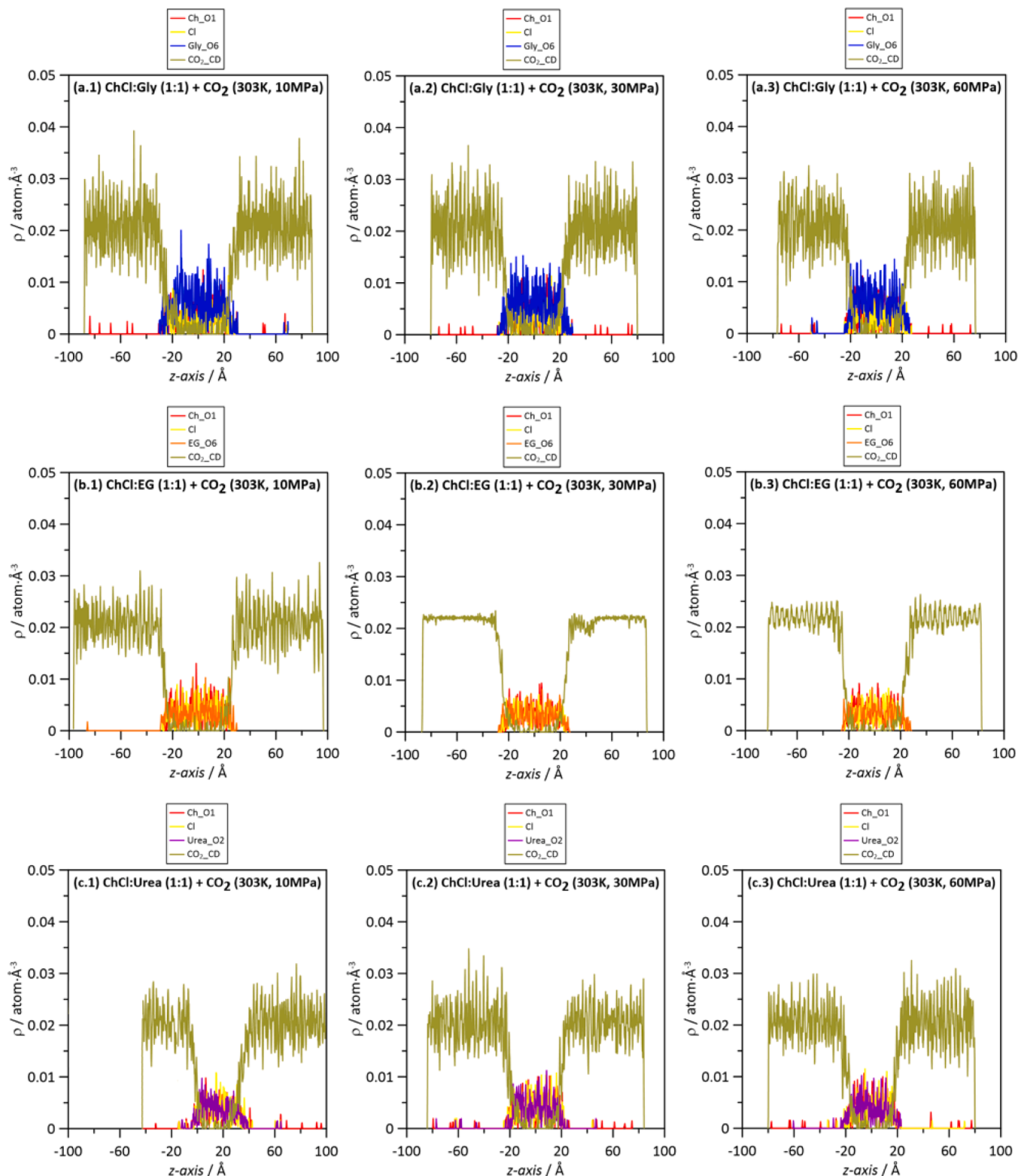


Fig. 18. Number density profiles, ρ , perpendicular to the interface for the considered DESs+CO₂ systems at 303 K and 10, 30 and 60 MPa.

The molecular-level insights complement the semi-empirical modeling results: the efficient interfacial transfer observed in simulations rationalizes the predominantly physical absorption mechanism inferred from CO₂ solubility correlations, while the uniform CO₂ distribution in bulk liquid justifies the use of equilibrium thermodynamics without explicitly accounting for kinetic or interfacial resistance effects. The temperature-induced broadening of the interface correlates with the

decreased CO₂ solubility at elevated temperatures, both reflecting weakened DES-CO₂ interactions. Together, these semi-empirical and MD modeling approaches provide a comprehensive, multiscale description of CO₂-DES systems, spanning molecular interactions to macroscopic phase equilibria.

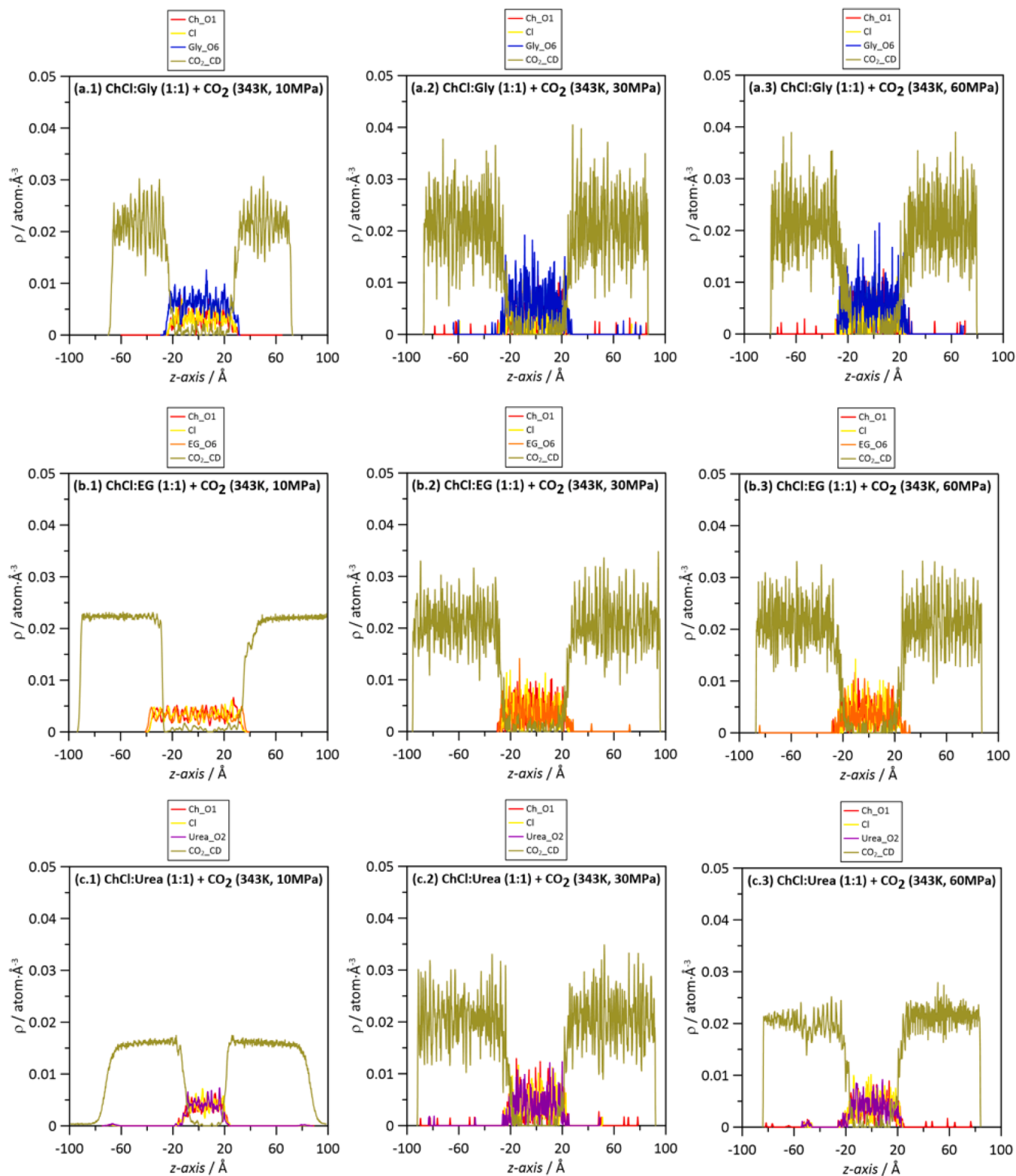


Fig. 19. Number density profiles, ρ , perpendicular to the interface for the considered DESs+CO₂ systems at 343 K and 10, 30 and 60 MPa.

4. Conclusions

This study presents an integrated semi-empirical and molecular modeling framework for predicting the thermophysical properties and CO₂ solubility of DESs over extended temperature and pressure ranges. The PHS EoS, combined with the RHST and ERT, successfully correlated and predicted density, isothermal compressibility, and viscosity for ten

DESs up to 100 MPa, achieving overall AARDs of approximately 0.3% for density, 3–5% for viscosity, and 3% for compressibility. These results demonstrate the capability of a physically grounded, low-parameter model to describe both equilibrium and non-equilibrium properties of complex hydrogen-bonded fluids with high accuracy.

Importantly, the results show that the observed macroscopic trends are governed by well-defined molecular mechanisms arising from the

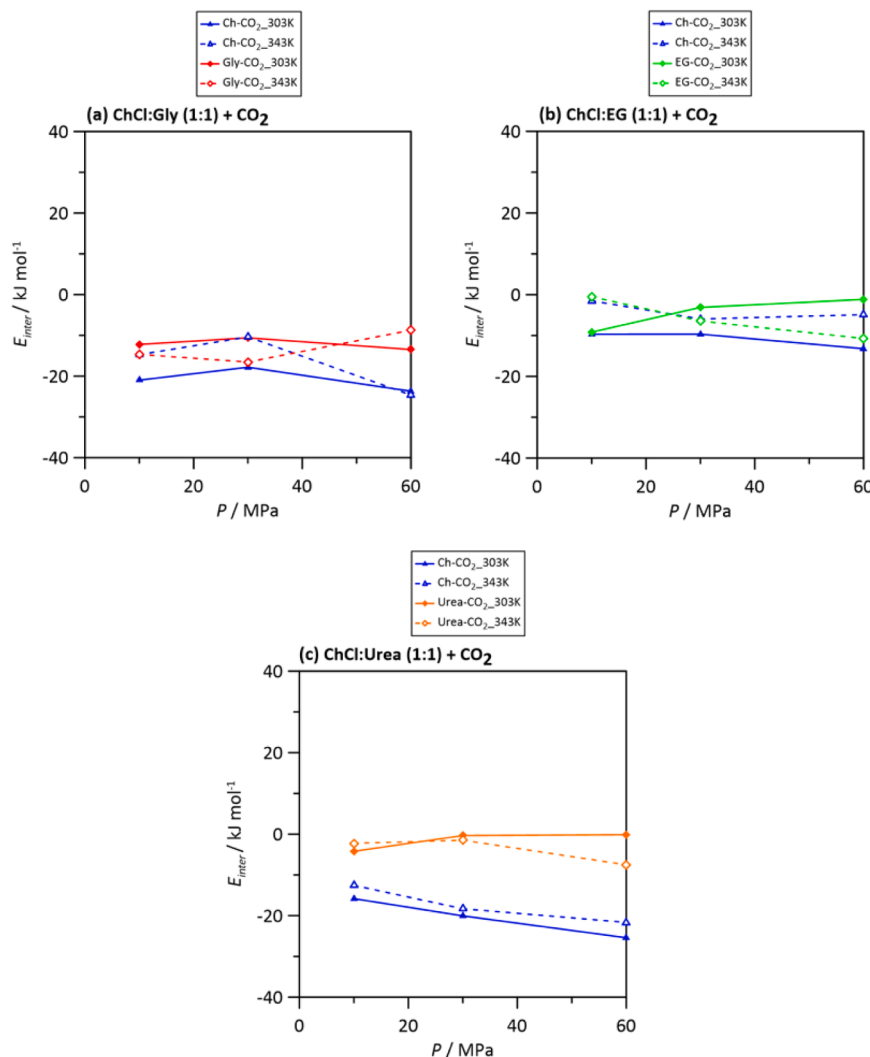


Fig. 20. MD intermolecular interaction energies between CO₂ and DESs components (sum of Lennard-Jones and coulombic contributions) for the considered DESs+CO₂ systems at 303/343 K and 10, 30 and 60 MPa.

interplay between hydrogen-bond network structure, polarity distribution, and molecular-level organization. Variations in σ -profiles capture changes in HBD and HBA contributions, which modulate the local solvation environment and determine the strength and specificity of solute-solvent interactions. Enhanced overlap between complementary σ -profile regions leads to enthalpic stabilization of the solvated state while simultaneously inducing a more ordered solvent arrangement, reflected in the associated entropic contributions. These effects collectively define the thermodynamics of solvation and rationalize the observed physico-chemical behaviour. Consequently, the present study provides a coherent mechanistic framework that links COSMO-RS descriptors, solvation thermodynamics, and molecular organization, moving beyond purely descriptive trends and offering molecular-level insights into the behaviour of the investigated systems.

The integration of the revised μ - μ approach with the PHS EoS provided a reliable description of high-pressure CO₂ solubilities in Reline, Glyceline, and Ethaline, yielding overall deviations below 10% from experimental data. The temperature dependence of the binary interaction parameter k_{ij} was found to reflect the strength and nature of CO₂-DES interactions, distinguishing between systems dominated by physical absorption and those exhibiting weaker associative contributions. These insights confirm that the semi-empirical model captures the balance between molecular-scale interactions and macroscopic solubility behavior.

MD simulations complemented the thermodynamic modeling by providing atomistic evidence for the persistence of hydrogen-bond networks, localized CO₂ stabilization sites, and the cooperative role of polar and aliphatic domains in determining viscosity and gas solubility. The consistency between simulation results and EoS predictions highlights the physical reliability of the proposed approach and reinforces the connection between molecular interactions and macroscopic observables.

Importantly, beyond providing structural interpretation and qualitative support, the MD simulations also offer guiding insight for the construction and refinement of the semi-empirical model. In particular, the identification and quantification of key molecular descriptors (such as density, self-diffusion coefficients or CO₂-DES interaction energies) enable a physically grounded interpretation of macroscopic properties (such as viscosity, CO₂ solubility or k_{ij}) and its variation across different DES systems and thermodynamic conditions. This reduces the purely empirical character of the model by linking its parameters to underlying intermolecular interactions and dynamic behavior. Moreover, the consistent temperature and pressure trends observed at the molecular level further support the robustness and transferability of the thermodynamic framework, reinforcing the role of MD simulations as an integral component of the multiscale modeling strategy.

Overall, this work establishes a transferable and computationally efficient framework for understanding and predicting the high-pressure

behavior of DESs. Beyond reproducing experimental data, the combined semi-empirical and molecular approach provides a predictive basis for the rational design of new solvent formulations with optimized viscosity, density, and CO₂ absorption capacity. Future research should extend this methodology to multicomponent gas systems, include temperature-dependent k_{ij} parameterization, and explore DES families containing hydrophobic or functionalized HBDs and HBAs to further enhance CO₂ selectivity and regeneration efficiency.

Abbreviations

ChCl:Gly (1:2)Glyceline
ChCl:Urea (1:2)Reline
ChCl:EG (1:2)Ethaline
OctOctanoic acid
CamCamphor
DcaDecanoic acid
DodcaDodecanoic acid
ThyThymol

CRedit authorship contribution statement

Alberto Gutiérrez: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Hoda Moslehi:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **Santiago Aparicio:** Writing – review & editing, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Hossein Said:** Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jcou.2026.103456](https://doi.org/10.1016/j.jcou.2026.103456).

Data Availability

Data will be made available on request.

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