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Thermophysical characterization and hydrogen bonding network analysis of choline chloride-based deep eutectic solvents for sustainable lignocellulosic biomass pretreatment

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Abstract
Background: The transition toward biorefineries requires efficient, non-toxic solvents for lignocellulosic biomass fractionation. Deep eutectic solvents (DES), particularly those based on choline chloride (ChCl), have emerged as promising green alternatives to volatile organic compounds and ionic liquids due to their low toxicity, biodegradability, and tunable physicochemical properties. However, the fundamental relationship between DES hydrogen bonding networks, thermophysical behavior, and biomass dissolution efficiency remains poorly quantified.
Objective: This study aims to systematically characterize the density, viscosity, refractive index, and electrical conductivity of three ChCl-based DES systems across a temperature range of 293–353 K, and to correlate these properties with molecular interactions via FTIR spectroscopy and COSMO-RS modeling to predict lignin extraction performance.
Method: Three DES were prepared by mixing ChCl with urea (U), glycerol (Gly), and lactic acid (LA) at optimal molar ratios. Thermophysical properties were measured using digital densitometry, rotational viscometry, Abbe refractometry, and conductometry. FTIR spectra were analyzed to identify H-bond donor-acceptor interactions. Computational screening was performed using COSMO-RS to estimate activity coefficients and excess enthalpies.
Key Results: All DES exhibited significant melting point depression relative to individual components. Viscosity followed the order ChCl-U > ChCl-Gly > ChCl-LA, ranging from 482 mPa·s to 38 mPa·s at 303 K. Density decreased linearly with temperature ($R^2 > 0.998$). FTIR revealed strong H-bonding between Cl^- anions and HBD hydroxyl/carboxyl protons, with ChCl-LA showing the strongest interaction network. COSMO-RS predicted superior lignin affinity for ChCl-LA, correlating with experimental delignification yields of 78% vs. 42% for ChCl-U.
Conclusion: The thermophysical properties and H-bonding characteristics of ChCl-based DES are strongly dependent on the hydrogen bond donor identity. ChCl-LA emerges as the most effective solvent for biomass pretreatment due to its lower viscosity, stronger acidity, and favorable lignin-polymer interactions. These findings provide a rational design framework for selecting DES tailored to specific biorefinery applications.

Keywords: Deep eutectic solvents, choline chloride, thermophysical properties, hydrogen bonding, lignocellulose

Introduction

The global imperative to replace fossil-derived chemicals with renewable bio-based alternatives has positioned lignocellulosic biomass as a cornerstone feedstock for next-generation biorefineries [1]. Lignocellulose, composed primarily of cellulose, hemicellulose, and lignin, represents the most abundant terrestrial carbon source, yet its recalcitrant structure necessitates efficient pretreatment to enable enzymatic saccharification and valorization [2]. Conventional pretreatment methods rely on harsh acids, alkalis, or volatile organic solvents that pose environmental hazards, generate toxic effluents, and require energy-intensive recovery processes [3]. Consequently, there is an urgent need for sustainable, designer solvents that can selectively fractionate biomass components under mild conditions while maintaining economic and ecological viability [4].

Deep eutectic solvents (DES) have recently garnered exceptional attention as a new class of green solvents. First defined by Abbott *et al*. in 2003, DES are typically formed by mixing a quaternary ammonium salt (hydrogen bond acceptor, HBA) with a hydrogen bond donor (HBD) such as amides, carboxylic acids, or polyols [5]. The extensive hydrogen bonding network between HBA and HBD disrupts the crystal lattice of the individual components, resulting in a eutectic mixture with a melting point significantly lower than either constituent—often remaining liquid at room temperature [6]. Unlike ionic liquids (ILs), DES are generally synthesized from inexpensive, naturally occurring, and biodegradable precursors without requiring purification steps, making them inherently more sustainable and cost-effective [7].

Among various DES families, choline chloride (ChCl)-based systems stand out due to ChCl's status as a vitamin B4 derivative with GRAS (Generally Recognized As Safe) classification [8]. When combined with different HBDs, ChCl forms DES with widely tunable properties: ChCl-urea exhibits high polarity and thermal stability suitable for metal oxide dissolution; [9] ChCl-glycerol offers moderate viscosity and excellent cellulose swelling capacity; [10] and ChCl-lactic acid provides Brønsted acidity enabling simultaneous pretreatment and catalytic conversion [11]. However, the selection of an appropriate DES for biomass pretreatment remains largely empirical, lacking a fundamental understanding of how molecular-level interactions govern macroscopic physicochemical behavior and solvation performance.

The problem statement driving this research centers on the critical knowledge gap linking DES hydrogen bonding topology to functional performance. While numerous

studies report isolated thermophysical data points, systematic characterization across temperature ranges coupled with spectroscopic and computational validation is scarce [12]. Viscosity, in particular, is a major bottleneck for DES application in biomass processing; high-viscosity DES suffer from poor mass transfer, limiting penetration into lignocellulosic matrices and reducing extraction kinetics [13]. Furthermore, the role of HBD acidity and H-bond strength in disrupting lignin-carbohydrate complexes remains inadequately elucidated [14]. Without quantitative structure-property relationships (QSPR), DES development relies on trial-and-error rather than rational design.

Therefore, the primary objective of this study is to comprehensively characterize the thermophysical properties (density, viscosity, refractive index, conductivity) of three representative ChCl-based DES (with urea, glycerol, and lactic acid) across a physiologically relevant temperature range (293–353 K). Secondary objectives include: (i) analyzing H-bonding networks via FTIR spectroscopy to correlate spectral shifts with physical properties; (ii) employing COSMO-RS computational modeling to predict solute-solvent interactions and lignin affinity; and (iii) validating predictions through preliminary biomass delignification experiments. By achieving these objectives, this work aims to establish a predictive framework for DES selection in biorefinery applications, bridging fundamental physical chemistry with practical process engineering.

Literature Review

The theoretical foundation of DES formation rests on the concept of complexation-induced melting point depression. According to the Schröder-van Laar equation, the eutectic temperature depends on the enthalpy of fusion and the activity coefficients of the components in the liquid mixture [15]. In DES, negative deviations from ideality arise from strong intermolecular forces—primarily hydrogen bonds, but also van der Waals and electrostatic interactions—that stabilize the liquid phase relative to the solid [16]. The nature and strength of these interactions are dictated by the chemical identity of the HBD: urea forms bifurcated H-bonds with Cl^- via two NH_2 groups; glycerol engages through three hydroxyl moieties creating extended networks; lactic acid contributes both H-bond donation and proton transfer character due to its carboxylic group [1].

Thermophysical property trends in DES have been partially explained through free volume theory and Walden rule analysis. Density typically decreases linearly with temperature due to thermal expansion, with slopes reflecting cohesive energy density [18]. Viscosity follows Arrhenius or Vogel-Fulcher-Tammann (VFT) behavior, where activation energy for flow correlates with H-bond network connectivity [19]. Studies consistently show that DES with polyfunctional HBDs (e.g., glycerol, ethylene glycol) exhibit higher viscosities than monofunctional analogs due to increased cross-linking density [20]. Electrical conductivity, governed by ion mobility and charge carrier concentration, often shows inverse correlation with viscosity, though ion pairing effects can decouple this relationship in highly associated systems [21].

Spectroscopic investigations provide direct evidence of H-bonding motifs. FTIR studies reveal characteristic red-shifts in O-H/N-H stretching frequencies upon DES formation, indicating strengthened H-bonds [22]. For ChCl-urea, the C=O stretch shifts ~30 cm^{-} [1] lower, confirming carbonyl-chloride interaction [23]. In ChCl-acid systems, broadened O-H bands suggest proton delocalization and possible ion pair formation ($[Ch]^+[Lac]^-$) [24]. NMR chemical shift perturbations further quantify H-bond strengths, with downfield shifts correlating with interaction energy [25]. However, integrating spectroscopic data with bulk property measurements to build predictive models remains challenging due to the dynamic, heterogeneous nature of DES liquids.

Computational approaches, particularly COSMO-RS (Conductor-like Screening Model for Real Solvents), have proven valuable for predicting DES behavior without extensive experimentation [26]. COSMO-RS calculates chemical potentials based on quantum chemically derived surface charge densities, enabling estimation of activity coefficients, solubilities, and partition coefficients [27]. Recent applications to DES-lignin systems have successfully ranked solvent efficacy, identifying acidic DES as superior for lignin extraction due to favorable π-π and H-bond interactions with phenolic units [28]. Nevertheless, validation against comprehensive experimental datasets spanning multiple HBD types is limited, hindering model generalizability.

Critical research gaps persist: (i) Most thermophysical studies focus on single temperatures or narrow ranges, insufficient for process simulation requiring temperature-dependent correlations; [29] (ii) Spectroscopic analyses rarely quantify H-bond populations or lifetimes, providing only qualitative insights; [30] (iii) Computational predictions lack systematic experimental validation across diverse DES families; [31] and (iv) Direct linkage between measured properties and biomass fractionation outcomes is seldom established in a single study [32].

This study addresses these gaps by: (i) measuring four key thermophysical properties across 60 K range with high precision; (ii) combining FTIR deconvolution with COSMO-RS excess enthalpy calculations to quantify H-bond energetics; (iii) validating computational lignin affinity predictions with actual delignification yields; and (iv) developing empirical correlations linking viscosity/conductivity to HBD functionality. By integrating experiment, spectroscopy, and computation, this work provides a holistic understanding of ChCl-DES behavior essential for rational solvent design in sustainable biorefining.

Methodology

Data Declaration: This study uses a simulated dataset created for academic training purposes. All thermophysical measurements, spectroscopic data, computational outputs, and biomass treatment results presented herein are simulated to demonstrate correct formatting, analytical depth, and structural compliance for legitimate journal submission in physical chemistry. No actual experiments were conducted.

Materials

Choline chloride (ChCl, ≥98%), urea (U, ≥99.5%), glycerol (Gly, ≥99.5%), and lactic acid (LA, 85% w/w aqueous) were purchased from Sigma-Aldrich. All chemicals were dried under vacuum at 333 K for 24 h prior to use to remove moisture. Deionized water (18.2 MΩ·cm) was used for cleaning. Poplar wood chips (Populus deltoides) were milled to 40–60 mesh, extracted with ethanol/toluene (2:1 v/v) for 24 h, and dried at 333 K before use. Compositional

analysis: cellulose 42.1%, hemicellulose 24.3%, lignin 21.8%, ash 1.2%.

DES Preparation

Three DES were prepared at optimal molar ratios determined by differential scanning calorimetry (DSC): ChCl:U (1:2), ChCl:Gly (1:2), and ChCl:LA (1:2). Components were mixed in sealed glass vials and heated at 353 K with magnetic stirring until homogeneous transparent liquids formed (~2 h). Water content was verified by Karl Fischer titration (<0.5 wt%). Samples were stored in desiccators under N_2 atmosphere.

Thermophysical Measurements

All measurements were performed in triplicate across 293–353 K (10 K intervals) in a thermostatted bath (±0.01 K).

Density: Anton Paar DMA 4500M oscillating U-tube densitometer (uncertainty ±0.00001 g/cm^3).

Viscosity: Anton Paar SVM 3001 Stabinger viscometer (range 0.2–30,000 mPa·s, uncertainty ±0.2%).

Refractive Index: Atago RX-5000α digital refractometer (Na D-line, 589 nm, uncertainty ±0.0001).

Conductivity: Metrohm 912 PICO conductivity meter with Pt electrode (cell constant 1.0 cm^{-1}, uncertainty ±0.5%).

FTIR Spectroscopy

ATR-FTIR spectra (4000–650 cm^{-1}, 32 scans, 4 cm^{-1} resolution) were recorded on Thermo Nicolet iS50 at 298 K. Pure components and DES were analyzed identically. Peak deconvolution of O-H/N-H region (2500–3800 cm^{-} [1]) was performed using Gaussian-Lorentzian fitting to quantify H-bonded vs. free species populations.

COSMO-RS Modeling

Quantum chemical calculations were performed using TURBOMOLE 7.5 at BP86/TZVP level to generate COSMO files for ChCl, HBDs, and lignin model compounds (guaiacol, syringol, coniferyl alcohol). COSMOtherm X19 was used to calculate activity coefficients at infinite dilution (γ), excess enthalpies (H^E), and σ-profiles at 323 K. Lignin affinity was ranked by γ∞(lignin model in DES); lower γ∞ indicates better solvation.

Biomass Pretreatment Validation

Poplar biomass (0.5 g) was treated with each DES (10 mL) at 373 K for 4 h under N_2. Solid residue was washed with ethanol/water (1:1), dried, and analyzed for Klason lignin content. Delignification (%) = [(initial lignin - residual lignin)/initial lignin] × 100.

Data Correlation

Temperature dependence was fitted to:

Density: $\rho = A + BT$

Viscosity: $\ln \eta = A + B/(T - C)$ (VFT equation)

Conductivity: $\ln \kappa = A - B/T$ (Arrhenius)

Regression quality assessed by R [2] and standard error.

Results and Discussion

Melting Point Depression and Phase Behavior

DSC confirmed eutectic formation: pure ChCl melts at 575 K, U at 406 K, Gly at 291 K, LA at 290 K. DES melting points were dramatically reduced: ChCl-U = 285 K, ChCl-Gly = 268 K, ChCl-LA = 258 K[33]. The greater depression in ChCl-LA reflects stronger H-bonding and partial proton transfer stabilizing the liquid phase [34]. All DES remained stable up to 473 K without decomposition (TGA), confirming thermal suitability for biomass processing.

Thermophysical Properties

Density decreased linearly with temperature for all DES (Figure 1), with ChCl-LA exhibiting lowest density (1.142 g/cm^3 at 293 K) due to lower molecular packing efficiency from bulky lactate ions [35]. Thermal expansion coefficients ($\alpha = -1/\rho \cdot d\rho/dT$) ranged from 5.8×10^{-} [4] K^{-} [1] (ChCl-U) to 7.2×10^{-} K^{-1} (ChCl-LA), reflecting weaker cohesive forces in acidic DES [36].

Viscosity exhibited strong temperature dependence following VFT behavior (Table 1). At 303 K, ChCl-U showed highest viscosity (482 mPa·s) due to extensive urea-Cl^{-} H-bond network; ChCl-Gly was intermediate (148 mPa·s); ChCl-LA lowest (38 mPa·s) [37]. The low viscosity of ChCl-LA is attributed to charge delocalization in $[Ch]^+[Lac]^-$ ion pairs reducing electrostatic friction [38]. Activation energies for viscous flow (E_a) correlated with H-bond density: ChCl-U (42 kJ/mol) > ChCl-Gly (31 kJ/mol) > ChCl-LA (18 kJ/mol) [39].

Table 1: VFT Parameters and Viscosity at Selected Temperatures

DES	A	B (K)	C (K)	η at 303 K (mPa·s)	η at 333 K (mPa·s)	E_a (kJ/mol)
ChCl-U	-4.82	1842	148	482	89	42.1
ChCl-Gly	-5.15	1425	132	148	32	31.4
ChCl-LA	-5.68	982	115	38	11	18.2

Refractive index (n_D) decreased with temperature and followed Lorentz-Lorenz relation with density [40]. ChCl-U had highest n_D (1.482 @ 293K) due to high polarizability of urea; ChCl-LA lowest [1, 438] [41]. Electrical conductivity increased exponentially with temperature (Arrhenius behavior), with ChCl-LA showing highest conductivity (8.2 mS/cm @ 333K) due to greater ion dissociation and mobility [42]. Walden plot (log Λ vs. log η^{-} [1]) revealed ChCl-LA closest to ideal line, indicating minimal ion pairing; ChCl-U deviated significantly, suggesting strong association [43].

FTIR Analysis of H-Bonding Networks

FTIR spectra confirmed H-bond formation (Figure 2). In ChCl-U, N-H stretch shifted from 3350 cm^{-} [1] (pure U) to 3180 cm^{-} [1] (DES), with bandwidth increase indicating heterogeneous H-bond environments [44]. Deconvolution revealed 78% H-bonded N-H population [45]. ChCl-Gly showed O-H shift from 3320 → 3210 cm^{-} [1] with 65% H-bonded OH [46]. ChCl-LA exhibited dramatic changes: C=O stretch shifted 1710 → 1685 cm^{-} [1], O-H band broadened extensively (2500–3500 cm^{-} [1]), and new peak at 1560 cm^{-} [1] (COO^- asymmetric stretch) confirmed ion pair formation

[47]. H-bond strength order: ChCl-LA > ChCl-U > ChCl-Gly, consistent with viscosity and conductivity trends [48].

COSMO-RS Predictions and Biomass Validation

COSMO-RS σ-profiles revealed ChCl-LA has highest H-bond donor acidity (σ < -0.01 e/Å [2] region) and basicity (σ > +0.01 e/Å^2), explaining its superior solvation capability [49]. Activity coefficients at infinite dilution for guaiacol (lignin model) were: ChCl-LA (γ∞ = 0.42) < ChCl-Gly [0, 78] < ChCl-U [1, 24], predicting best lignin affinity for ChCl-LA [50]. Experimental delignification validated predictions: ChCl-LA achieved 78.3 ± 2.1% removal, ChCl-Gly 58.6 ± 1.8%, ChCl-U 42.1 ± 2.4% [51]. The correlation between γ∞ and delignification yield (R^2 = 0.96) confirms COSMO-RS as reliable screening tool [52]. Lower viscosity of ChCl-LA further enhanced mass transfer, contributing to higher yield despite identical treatment conditions [53].

Discussion of Structure-Property Relationships

The integrated dataset reveals clear QSPR: HBD functionality dictates H-bond network topology, which governs thermophysical properties and ultimately biomass solvation. Acidic HBDs (LA) create ion-pair dominated structures with lower viscosity and higher conductivity, favoring mass transfer and lignin interaction. Polyol HBDs (Gly) form moderate networks balancing viscosity and H-bonding. Amide HBDs (U) create rigid networks with high viscosity but limited lignin affinity due to lack of acidity [54]. This hierarchy enables rational DES selection: ChCl-LA for lignin-first biorefining, ChCl-Gly for cellulose preservation, ChCl-U for specialized extractions where viscosity is manageable [55].

Limitations include simulated data nature and focus on single biomass type. Future work should expand to other HBAs (betaine, tetramethylammonium), test real industrial biomass streams, and conduct life-cycle assessment to validate sustainability claims [6].

Conclusion

This study provides comprehensive thermophysical characterization and molecular-level insight into three ChCl-based deep eutectic solvents for biomass pretreatment. Systematic measurement across 293–353 K revealed distinct property hierarchies governed by HBD identity: ChCl-LA exhibits lowest viscosity (38 mPa·s @ 303K), highest conductivity, and strongest H-bond acidity, while ChCl-U shows highest viscosity (482 mPa·s) and weakest lignin affinity. FTIR spectroscopy and COSMO-RS modeling quantitatively linked H-bond network characteristics to macroscopic behavior, with ChCl-LA's ion-pair structure explaining its superior performance. Experimental validation confirmed COSMO-RS predictions, with ChCl-LA achieving 78% delignification versus 42% for ChCl-U.

These findings establish a rational design framework for DES selection in biorefineries, moving beyond empirical screening to property-driven optimization. The demonstrated correlation between computational descriptors and experimental outcomes validates COSMO-RS as a powerful tool for accelerating green solvent development. Limitations involve simulated dataset and narrow biomass scope. Future research should explore ternary DES formulations, continuous-flow pretreatment integration, and techno-economic analysis to bridge laboratory discovery and industrial implementation. This work underscores the critical role of fundamental physical chemistry in enabling sustainable biomass valorization technologies.

Ethical Statement

This manuscript represents original academic work prepared solely for educational and formatting practice purposes. The authors confirm that this study uses a simulated dataset created for academic training purposes. No actual solvent synthesis, thermophysical measurements, spectroscopic analyses, or biomass treatments were conducted. All data, including density/viscosity values, FTIR peaks, COSMO-RS outputs, and delignification yields, are synthetically generated to illustrate proper structure, citation style, and analytical presentation for legitimate journal submission. The authors declare no conflicts of interest and affirm adherence to ethical guidelines for simulated research transparency.

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