



Measurements of thermodynamic properties and activity coefficients at infinite dilution of selected organic solutes and water in a deep eutectic solvent (choline chloride +1,3 propanediol)

Banzi P. Mbatha^a, Peterson T. Ngema^a, Suresh Ramsuroop^b, Kaniki Tumba^c,
Lindokuhle Manyoni^a, Nkululeko Nkosi^{d,*}

^a Department of Chemical Engineering, Chemical Thermodynamics Research Group, Durban University of Technology, Steve Biko Campus, Durban 4001, South Africa

^b Cape Peninsula University of Technology, Department of Chemical Engineering, Bellville Campus, Bellville 7535, South Africa

^c School of Chemical and Minerals Engineering, Faculty of Engineering, North-West University, Potchefstroom Campus, 2351, South Africa

^d Department of Chemical Engineering, Thermodynamics, Materials and Separations Research Group (TMSRG), Mangosuthu University of Technology, uMlazi, Durban 4031, South Africa

ARTICLE INFO

Keywords:

Deep eutectic solvent
Infinite dilution activity coefficient
Selectivity
Partial molar excess properties
Intermolecular interactions, 1,3 Propanediol

ABSTRACT

In this study, a deep eutectic solvent (DES) consisting of choline chloride (ChCl) and 1,3 propanediol (Pdiol) at a 1:2 M ratio was evaluated experimentally for its extractive efficiency. The important DES's physicochemical properties: density, viscosity, and refractive index, were measured at $T = (293.15\text{--}353.15)$ K and 101.3 kPa. Solvent intermolecular interaction strengths against 32 selected organic solutes were assessed using experimental infinite dilution activity coefficients (IDAC) measured at $T = (313.15\text{ to }343.15)$ K and 101.3 kPa. The interactions between the solute and solvent molecules were further characterised by partial molar excess properties ($\Delta H_i^{E,\infty}$, $\Delta G_i^{E,\infty}$ and $T_{ref}\Delta S_i^{E,\infty}$). The separation ability of the solvent was assessed using selectivity (S_{ij}^{∞}) and capacity (k_j^{∞}) as thermodynamic separation parameters. DES indicated stronger interactions with more polar molecules. The findings indicate that DES is suitable for separating the alkanes from alcohols, acetonitrile or thiophene mixtures. This work adds to the DES database and offers a theoretical framework for industrial separation problems.

1. Introduction

Separating azeotropic or close-boiling mixtures has generally been one of the most challenging tasks in industrial processes since they are basically impossible to separate by distillation and require operating conditions of high temperature, pressure, and energy. In practice, the physical separation of these mixtures is carried out through liquid-liquid extraction (LLE) or extractive distillation, depending on their compositional range, since the products must be recovered at specific purities [1–4]. Chemical industries use these industrial technologies because they can handle bulk volumes and recover components in relatively pure forms [1–4]. These technologies, however, are highly energy-intensive, accounting for more than 40 % of the total energy used by the chemical plant. The solvent's volatile nature and the requirement for downstream processes to purify and recover the solvent lead to increased process costs and high operational risks. Indirectly, these technologies' organic

volatile solvents (VOCs) are causing global warming and atmospheric variability, causing huge incompatibilities between people and sustainability [5,6]. Likewise, these issues threaten prosperity, security, and the health of humans and the environment [5,7].

Undoubtedly, industrial VOC emissions adversely affect humans and the environment. A WHO report published in 2021 estimated that outdoor pollution caused 7.0 million premature deaths attributed to air pollution, with 99 % of the world's population living in poor air quality [7]. Developing economies have a growing energy demand; hence, industrial VOC challenges continue. VOCs also pose a hindrance because of their low separation capability and requirement for larger quantities. A sustainable environment and emerging clean technology based on eco-friendly technology are becoming increasingly important as environmental concerns rise. It is crucial to choose green media that meet the standard criteria in green chemistry and technology; they must be nontoxic, biodegradable, cheap, environmentally friendly, and

* Corresponding author.

E-mail address: nkosi.nkululeko@mut.ac.za (N. Nkosi).

<https://doi.org/10.1016/j.molliq.2025.128320>

Received 15 April 2025; Received in revised form 1 August 2025; Accepted 10 August 2025

Available online 15 August 2025

0167-7322/© 2025 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

biocompatible. Deep eutectic solvents (DES) and ionic liquids (ILs) are examples of environmentally friendly media [8–11].

As a possible substitute for volatile organic compounds needed in numerous extractive processes, ILs could be considered a more environmentally friendly and feasible option [12,13]. Complex synthesis, high prices, and toxicity issues limit ILs' application in industrial processes [14]. Green chemistry is concerned with reducing pollution as much as possible in raw materials and production processes [15]. Contrary to popular belief, these neoteric solvents' "green credentials" are now strongly contested in the scientific literature [15]. It has been noted in many reports that ILs present a hazardous level of toxicity, as well as poor biodegradability [16,17]. The physical properties of ILs are also affected by impurities, even if they are present in trace amounts. The synthesis of these compounds is also far from eco-friendly since large quantities of salts and solvents are usually required to exchange their anions completely. ILs suffer from these drawbacks, and their high cost hinders their industrial application [13]. New concepts are therefore required to make better use of these systems.

In this case, DESs consisting of a hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) offer a better advantage in overcoming these cited IL challenges. This is because DESs can also be prepared with two environmentally friendly ingredients that are abundant in nature, thus making these DESs "green" solvents. A combination variation of HBDs and HBAs can be used to control the properties of DES-like mixtures. DES's higher viscosity than that of water, cited in the literature as one of its drawbacks, can also be improved by adjusting the molar ratios or composition. Through this adjustment, DES properties (such as polarity, density, conductivity, stability, and viscosity), strongly influenced by hydrogen bonding interactions, are tuned and made more favourable [18–20]. However, optimising their physical properties is crucial to making solvent extractive processes more commercially profitable.

Prior to this, one can consider the availability and costs of materials used in the production of HBA and HBD, along with their toxicity levels, when choosing DES mixtures. Some DES combinations have been observed to follow this selection criterion, including ChCl + Urea, ChCl + alkane-triol, ChCl + alkane-diol and ChCl + simple sugar mixtures [18,20–23]. DESs derived from ChCl + Urea, ChCl + alkane-triol, and ChCl + alkane-diol mixtures are the most studied solvents in extraction techniques, such as liquid-liquid extraction and extractive distillation. Glycerol, also a triol, is too viscous (1500 mPa.s at $T = 293.15$ K), a major hindrance to its use as a solvent extraction agent. In the same way, urea, an amide, even though it solidifies at 406.15 K, which does not prevent its application in extraction processes, poses an environmental problem since it hydrolyses to produce corrosive ammonia. In addition, its pure form or use as an HBD in DESs with a higher molar ratio may cause technical failures in the extraction process, such as salt precipitation leading to fouling or clogging of liquid-liquid extraction columns, reduced mass transfer efficiency, and corrosion issues in extractive distillation equipment. ChCl + ethylene glycol mixture appears to offer viscosities that are closer to water. Diols like ethylene glycol (21.62 mPa.s at $T = 293.15$ K) are less viscous than glycerol and urea and, because of intermolecular hydrogen bonding, can form dimers (possibly chains or clusters), which could make them useful for extraction processes. The fact that ethylene glycol is thermodynamically stable in different conformations, such as *trans* and *gauche*, explains its tendency to form dimers. As a result of the hydrogen-bond network in alkane-diol-based DES, all the viscosity, melting point, density, dynamics, and charge transport properties are positively influenced.

Alkane-diol-based DES's physicochemical properties have been extensively studied [18–21,23–26]. The influence of alkane-diol DESs on extractive efficiency in selected industrial separation problems has been investigated by a few researchers by measuring the activity coefficients at infinite dilution (γ_{13}^{∞}) of DESs and by looking at the effects of alkane-diol DESs containing ChCl as an HBA on extractive efficiency. As few studies have reported on alkane-diol DESs containing ChCl, the

present study fills this gap. One can understand how DES interacts with solutes by measuring the thermodynamic properties of various probes in alkane-diol DES and analysing the infinite dilution activity coefficient (IDAC) data. For industrial applications, IDAC data can provide excellent pre-screening data for extraction solvents. A low γ_{13}^{∞} value is usually observed for alkynes, polar substances such as alcohols, ketones or ethers resulting from hydrogen bonds, the π - π , n - π , or other strong interactions. Recent studies of the DESs measured up to 2022 were reviewed by Mgxadeni and co-workers [27], providing a thorough literature review and highlighting research gaps.

In this context, the present study aims to investigate the extractive efficiency of DES based on ChCl and 1,3 propanediol (1,3 Pdiol) at a molar ratio of 1:2 as a possible replacement of VOCs as extractant solvents. This mixture is consistent with the eutectic compositions reported by Silva et al. [28]. According to the current literature, the molecular structure of DES precursors can be an essential factor in determining how intermolecular interactions can be influenced economically and sustainably [29]. One of the key objectives of this research is to understand how the hydrogen bonding network of ChCl and 1,3 Pdiol is influenced by the system temperature and how the results affect solvent properties, which will help verify its potential application and recovery. To assess the solvent extractive efficiency of 1,3 Pdiol, we compare our obtained data with extensively studied DES systems, culminating in proposals to broaden the range of DES systems.

2. Methods section

2.1. Materials

A table with specifications of each solute, gas carrier, and DES compound used in this study is provided as part of the supplementary materials in **Table S1**. Since the gas-liquid chromatograph (GLC) separated impurities on the column, all solutes were used without further purification. DES was prepared using ChCl (HBA) and 1,3 Pdiol (HBD). A vacuum oven drier, model FSOM 4 (supplied by Labcon), at 313.15 K (for 24 h) was used to remove excess moisture absorbed from ambient humidity from HBA and HBD after degassing under a high vacuum (10^{-4} bar). The DES molecules used in this study are shown in **Fig. 1**. Shinwasorb-S 80/100 mesh support material (for use as adsorbent) was vacuum purified at 363.15 K for 6 h to remove any moisture absorbed. It was provided by Shinwa Chemical Industries (Japan). Dichloromethane was used as a dispersion promoter. Helium was used as the carrier gas in the GLC.

2.1. Experimental procedures

2.2.1 Preparation of DES

DES was prepared according to a method described in previous studies [30]. A 1.000:1.999 M ratio was used in the mixing of HBA and

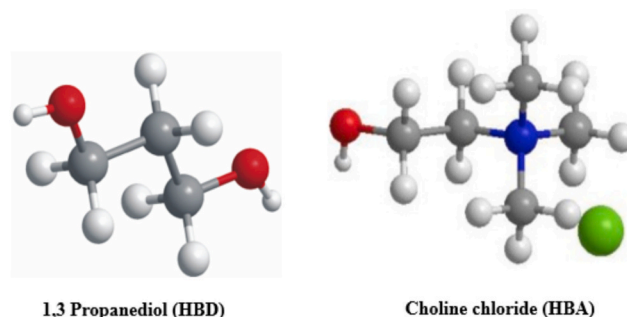


Fig. 1. Chemical structure of HBA and HBD compounds.

HBD. Masses of HBA and HBD corresponding to this molar ratio were prepared in a 20 mL sealable sample vial using an accurate analytical balance, model AS220/C/2 (supplied by RADWAG) with an uncertainty of 0.0001 g in mass to prepare a mixture with an uncertainty level of 0.5 mg gravimetrically. The sample vial containing the mixture was immediately sealed tightly and stirred using a magnetic stirrer at 353.15 K for approximately 2 h. DES was then placed in a vacuum oven dryer and kept at 323.15 K for 8 h to remove moisture, cooled in a desiccator, and stored in a sealed container away from natural light. The compositional uncertainty in the molar fraction of each DES component was 0.01 mol%.

2.1.1. Water content

A Karl-Fischer moisture titrator (870 KF Titrino Plus, Metrohm, South Africa) was used to determine the water content of HBA, HBD, and DES. These compounds were dissolved in methanol and titrated in steps of 0.009 mL. In this procedure, DES was kept below 1000 ppm, a level recommended by diverse authors for thermophysical properties measurements. Approximately 440, 570, and 230 ppm of water contents were found in the HBA, HBD, and DES (standard uncertainty: 50.0 ppm).

2.1.2. Density, viscosity and refractive index measurement

The density (ρ), refractive index (RI), and viscosity (μ) of DES have been measured at atmospheric pressure at temperatures of (298.15–343.15) K in accordance with previous investigations [31,32]. Measurements of these thermophysical properties were obtained in an integrated system composed of an Atago refractometer (Midrand, SA) model RX-7000 (with an uncertainty of 0.0001), Anton Paar densimeter (Midrand, SA), model DSA 5000 M (with an uncertainty of 0.0001 g/cm³) and Anton Paar AMVn rolling-ball viscometer (Midrand, SA). Calibration of the densimeter, refractometer, and viscometer at 298.15 to 323.15 K and 101.3 kPa was done before measuring thermophysical properties to ensure these pieces of equipment produced valid results. Ultrapure Millipore water obtained from the Millipore-Q system (Fusion 320 model) supplied by SUEZ with an electrical resistivity of 18.2 M Ω cm at 298.15 K was used to calibrate the densimeter. Calibration of the refractometer was performed with ultrapure Millipore water. Capillaries of calibrated glass diameters of 1.59, 1.80, and 2.50 mm were used to measure the dynamic viscosity of ultrapure Millipore water using the falling ball principle. A viscosity standard provided by Anton Paar was used to calibrate the capillaries. NIST-certified fluid standards data were used to validate and confirm calibration procedures [33–36]. For measurements of DES viscosities, a capillary with a diameter of 1.80 mm was used. An average of three readings was taken for each temperature to ensure reliability, reproducibility, and accuracy of the measured DES densities, viscosities, and refractive indices. This study measured refractive index data at a wavelength of 589.3 nm. As shown in Table S2, there is reasonable agreement between the calibration data and the reported literature data for the water system. Calibration uncertainty for viscosity, density, and refractive index was 0.00013 (0.01 %) mPa.s, 0.00003 (0.003 %) g/cm³, and 0.00001 (0.001 %). DES thermophysical properties were determined at temperatures (298.15 to 343.15) K with intervals of 5 K using the same instruments. For reported DES thermophysical properties, a relative standard uncertainty of 3.0 % was obtained for viscosity, and 1.7×10^{-3} g/cm³ and 1.4×10^{-3} for density and refractive index, respectively. A good agreement is observed between the thermophysical properties measured in this study (as shown in Table 1) and those reported in the literature [19,37,38].

2.1.3. Fourier transform infrared (FT-IR) spectroscopy analysis

A Fourier transform infrared spectrometer (FT-IR) model Tensor 27 (Bruker, USA) equipped with an ATR accessory and OPUS software was used to identify the chemical functionalities of the HBA, HBD, and DES. Data was collected using Nicolet Omnic infrared spectroscopy software (version 8.0) in the 4000 to 600 cm⁻¹ range, with a resolution of 4 cm⁻¹ and spectra were averaged over 32 scans to ensure spectral clarity. Data

Table 1

DES's [ChCl +1,3 Pdiol, with the molar ratio of ChCl to 1,3 Pdiol of 1:2] density (ρ), viscosity (μ), and refractive index (RI) as a function of temperature and atmospheric pressure at 101.3 kPa.^a

T/K	ρ /g.cm ⁻³	μ /mPa.s	$RI^{\dagger}$
298.15	1.0849	62.163	1.4677
303.15	1.0809	51.360	1.4657
313.15	1.0761	35.514	1.4634
323.15	1.0709	24.413	1.4609
333.15	1.0656	18.744	1.4585
343.15	1.0602	–	1.4559

^a Standard uncertainties u (0.68 level of confidence) are $u(\rho) = 1.7 \times 10^{-3}$ g/cm³, $u(RI) = 1.4 \times 10^{-3}$, $u(T) = 0.01$ K, $u(p) = 2.0$ kPa and $u(\text{DES molar ratio}) = 0.006$. Relative standard uncertainty $u_r(\mu) = 3.0$ % of measured values. [†] Wavelength (λ) = 589.3 nm.

analyses were performed using ORIN8.0 software. Solid samples were prepared in potassium bromide (KBr) pellets before infrared illumination, while liquid samples were cold-pressed between two KBr plates to form films for transmission measurements. Baseline correction and normalisation (at 1600 cm⁻¹) were applied as post-treatment to the spectra. Spectra from each sample were collected only once.

2.1.4. Nuclear magnetic resonance (NMR) spectroscopy analysis

Spectral nuclear magnetic resonance (NMR) measurements were performed to gain more insight into HBD, HBA, and DES, and to identify the chemical functionalities. The samples for NMR analysis were prepared by weighing and inserting 20 to 30 mg of HBD, HBA, and DES into the 5 mm tubes. A volume of 700 μ L dimethyl sulfoxide (DMSO) was used as a solvent to dissolve these samples overnight under agitation (room temperature). In this case, DMSO was used as an internal reference. A Bruker Avance Neo 500 MHz type spectrometer (supplied by Bruker Corp., SA) was used for ¹H NMR analyses. Spectra were obtained using 16 scans at a resolution of approximately 0.1 ppm. A Bruker pulse software, TopSpin, was used to analyse the data (with pre-saturation to remove the water signals from spectra). Existing databases were used to assign proton resonances to the data.

2.1.5. Activity coefficient measurements

A Shimadzu GC-2014 gas chromatograph equipped with a thermal conductivity detector was used for the IDAC experiments. Two 0.5 m long stainless columns with an inner diameter of 4.1 mm were fitted in the GC, containing Shinwasorb-S (80/100 mesh) and helium gas as stationary and mobile phases, respectively. In this study, column preparation and packing were performed according to methods previously described in the literature [31,32]. Initially, both columns were cleaned with hot soapy water, rinsed with cold water, and flushed with acetone to shorten drying times before packing with solid support (Shinwasorb-S). The prepared DES was added to the pre-weighed amount of Shinwasorb-S in the round-bottom flask. Dichloromethane was added to the round-bottom flask as a dispersion promoter to assist with coating the solid support with the prepared DES. Dichloromethane was evaporated through the use of a vacuum pump. After drying, the mixture was placed in an oven drier set at 333.15 K for additional drying. An 8-h conditioning process was performed at 333.15 K to remove dichloromethane from the packed column. The percentage mass fractions of DES used in the solvent column were 27.37 and 33.07. The experimental flow rate was measured at 10 and 20 mL/min using a bubble flowmeter placed after the thermal conductivity detector. Volumes of solutes injected ranged from 0.2 to 0.3 μ L. The injector and detector were set at $T = 523.15$ K, which was above the boiling point of all solutes used in this study. An electronic barometer was used to measure the outlet pressure and the ambient temperature. A minimum of three repetitions were performed for each temperature (313.15, 323.15, 333.15, and 343.15) K to ensure the reproducibility of the measurements.

2.2. Testing and validation of the GLC technique

A GLC technique was validated using hexadecane as a stationary phase and *n*-hexane, cyclohexane and benzene as solutes at 313.15 K and 101.3 kPa. In our previous work [31], we reported the test system data using the same column. Experimental data for test systems (*n*-hexane, cyclohexane and benzene) reported in **Table S3** demonstrated acceptable deviations (5.53, 3.17 and 2.61 %, respectively) against data from the literature. It was determined that the GLC technique used is reliable by comparing the obtained results' relative error with those reported in the literature [39–45].

3. Thermodynamic theoretical calculation

Infinite dilution activity coefficients: Solute's (1) IDAC data in solvent (3) was determined using eq. 1 below [46]:

$$\ln \gamma_{13}^{\infty} = \ln \left(\frac{n_3 RT}{V_N P_1^*} \right) - \frac{(B_{11} - v_1^*) P_1^*}{RT} + \frac{(2B_{12} - v_1^{\infty}) J_2^3 P_o}{RT} \quad (1)$$

where γ_{13}^{∞} , n_3 , R , V_N , P_o and P_1^* , respectively, denote the activity coefficient of solute (1) at infinite dilution in the stationary phase (3), number of moles of DES in the column packing, ideal gas constant; net retention volume of solute obtained in Eq. 2; column outlet pressure which is equal to the atmospheric pressure; saturated vapour pressure of the solute (1) at temperature T , obtained through Antoine equation [47,48]. The second and third terms serve as the correctional terms for the nonideality of the mobile phase at effect pressure. B_{11} and B_{12} are the second virial coefficient of the pure solutes (1) and cross virial coefficient between the solute (1) and carrier gas (2), respectively [49,50]. v_1^* and v_1^{∞} are the molar volume of the solute (1) and partial molar volume of the solute at infinite dilution in the solvent ($v_1^* \cong v_1^{\infty}$), respectively. J_2^3 denotes the pressure correction factor obtained in Eq. 3 [46]. The parameters used to determine γ_{13}^{∞} were obtained from various thermodynamic tables, given by [47,48].

The net retention volume of the solute (1) V_N , was determined using the following equation given by [51]:

$$V_N = (J_2^3)^{-1} U_o (t_R - t_G) \frac{T_{col}}{T_f} \left(1 - \frac{P_w^*}{P_o} \right) \quad (2)$$

where t_R , t_G , U_o , T_{col} , T_f , and P_w^* , respectively, denote the retention time for the solute, the retention time for the unretained gas, the flow rate of helium gas measured at the column outlet using a bubble flow meter, column temperature, flow meter temperature, and the saturated vapour pressure of water at T_f . The modified Antoine or Wagner equations were used to calculate saturated vapour pressures for all solutes based on their applicability ranges [47,48]. The pressure correlation term is given by Everett, 1965, as follows:

$$J_2^3 = \left(\frac{2}{3} \right) \left[\frac{\left(\frac{P_i}{P_o} \right)^3 - 1}{\left(\frac{P_i}{P_o} \right)^2 - 1} \right] \quad (3)$$

where P_i and P_o denote the pressure inlet and outlet at the column of the GC.

Using thermodynamic functions, we further evaluated the impact of temperature on intermolecular interactions and IDAC values. This is to clearly assess the effect of changing the system temperature on the dissociation of the solute and the required energy to break its interaction with the solvent. In this case, the excess partial molar enthalpy ($\Delta H_i^{E,\infty}$), excess partial molar Gibbs energy ($\Delta G_i^{E,\infty}$), and excess partial molar entropy ($T_{ref} \Delta S_i^{E,\infty}$) at infinite dilution for all organic solutes in DES were calculated by decomposing $\ln \gamma_{13}^{\infty}$ in eq. (1) into these thermodynamic functions. From eq. (1), $\ln \gamma_{13}^{\infty}$ could be split into its respective $\Delta H_i^{E,\infty}$ and

$T_{ref} \Delta S_i^{E,\infty}$ contributions:

$$\ln \gamma_{13}^{\infty} = \frac{\Delta H_i^{E,\infty}}{RT} - \frac{\Delta S_i^{E,\infty}}{R} \quad (7)$$

From the slope and intercept of the linear temperature dependence, we calculated the two thermodynamic properties ($\Delta H_i^{E,\infty} = Ra$ and $\Delta S_i^{E,\infty} = -Rb$) as follows:

$$\ln \gamma_{13}^{\infty} = \frac{a}{T} + b \quad (8)$$

In eq. (8) above, a represents the slope, and b represents the intercept. From the equation below, partial molar excess Gibbs energies were calculated [52]:

$$\Delta G_i^{E,\infty} = RT \ln(\gamma_{13}^{\infty}) = \Delta H_i^{E,\infty} - T_{ref} \Delta S_i^{E,\infty} \quad (9)$$

This equation reflects different interactions between solutes and solvents and the change in enthalpy and entropy during the dissolution process, as shown in Gibbs–Helmholtz Eq. (9).

Gas-liquid partition coefficient (K_L), which are determined by the thermodynamic properties of the solute in the two phases, play an important role in gas-liquid partition chromatography. For the K_L to be determined, DES density must be known. The gas-to-liquid partition coefficient, $K_L = C^L/C^G$ for a solute (1) partitioning between a carrier gas (2) and a solvent (3) was calculated from solute retention data according to the following Eq. (10):

$$\ln K_L = \ln \left(\frac{V_N \rho_3}{m_3} \right) - \frac{P_o J_2^3 (2B_{12} - V_1^{\infty})}{RT} \quad (10)$$

where m_3 denotes the mass of DES in the column packing.

4. Results and discussion

4.1. Formation, verification and functional group analysis of DES and precursors

In this study, the prepared DES was assessed if it met the first basic criterion of solvent for IDAC measurements (must be in liquid state at experimental temperature ranges) prior to its use for further research. After cooling prepared DESs (1:1 and 1:2 M ratios) to room temperature, DES formed at a 1:1 M ratio solidified. In contrast, a molar ratio of 1:2 was a colourless, transparent liquid at room temperature and experimental temperature ranges. This leads to the conclusion that a 1:1 M ratio is not recommended for DES-based separation processes governed by liquid–liquid or vapour–liquid equilibria. Therefore, the sample was discarded for further consideration in this study. On the other hand, selected DES (1:2), which forms a liquid at room temperature, is easy to handle for intended practical applications. This ratio will be more practical for liquid–liquid system applications. In this case, the system should be at a temperature as far as possible from freezing. Functional groups should exist in their original forms when DES is formed, as no chemical reactions occur during preparation. This observation was confirmed using two analytical methods: FT-IR and NMR spectroscopy. These analytical methods were used to check the characteristic functional groups of the HBD and HBA present, and to confirm their presence in the resulting DES. **Figs. S1, S2 and S3** present the FT-IR and NMR spectra of the HBD, HBA and the formed DES, respectively.

1,3 Pdiol (**Fig. S1a**) FT-IR spectra show a characteristic stretching vibration peak at 2989 to 3601 cm^{-1} associated with the hydroxyl group, while the symmetric bending vibration peak of the carbon-hydrogen Sp^3 bond, which is more defined and wider than that of ChCl, is at 2982 to 2777 cm^{-1} . FT-IR spectra of ChCl (**Fig. S1b**) show a characteristic stretching vibration peak at 1480 cm^{-1} for methyl groups of the trimethyl ammonium $(\text{CH}_3)_3\text{N}^+$ ion, 1081 cm^{-1} for carbonyl ($\text{C}=\text{O}$) groups and 1141 cm^{-1} for N^+Cl^- (quaternary ammonium or $\text{C}-\text{N}$ groups). A symmetric bending vibration peak of CH_3 is located at 2948

to 3038 cm^{-1} , and a stretching vibration peak of OH is located at 3038 to 3616 cm^{-1} . The peak with 950 cm^{-1} wavenumber can be attributed to the C–N group from the choline chloride. The results are consistent with those of the NIST database and literature [18,53–57]. The shifts in wavenumbers of DES compared to its precursors can indicate molecular interactions that occurred in its formation (Fig. S1c). The absorption peaks of C=O and OH have shifted from their original positions. The C=O and OH groups shifted to 1133 and 3298 cm^{-1} , respectively. An explanation for this observed behaviour is the molecular interaction between the 1,3 Pdiol OH group and the one from ChCl that stretches the protons in the OH group. A shift of the N^+Cl^- absorption vibration peak of ChCl in DES from 1141 to 1170 cm^{-1} has also been observed. This phenomenon shows that DES is formed by hydrogen bonds between C=O on 1,3 Pdiol and N^+Cl^- on ChCl. The FT-IR analysis proves that DES components form the eutectic mixture, and there is no sign of a chemical reaction. We examined ^1H NMR (Figs. S2 and S3) as an alternative method for assessing intermolecular interactions to validate this conclusive statement. Fig. S3 shows that the ChCl and 1,3 Pdiol peaks in deuterated DMSO are chemically shifted, reflecting changes in the electronic environment due to hydrogen bonding. ChCl peaks appear only at 3.1397 (9H, Hd), 3.3913–3.4479 (m, 2H, Hc), 3.8905 (m, 2H, Hb) and 54,395–5.4561 (m, 1H, Ha). Chemical shifts for 1,3 Pdiol are 1.5008–1.5436 (m, 2H, H1), 3.7972 (m, 1H, H1a) and 4.6000–4.6171 (m, 2H, H2).

4.1. Physico-chemical properties of DES

This study measured the solvent's thermophysical properties (density, viscosity, and refractive index) for prepared DES at temperatures ranging from 293.15 to 343.15 K at a pressure of 101.3 kPa. A thermophysical property such as density or viscosity is crucial to any application's design, operation, and optimisation. To the best of our knowledge, information about the measured thermophysical properties of alkane-diol-based DES at a molar ratio of 1:2 within the considered temperature range is still scarce [58,59]. Conversely, very few studies reported the thermophysical properties of alkane-diol-based DESs. These studies reported density and viscosity values for alkane-diol-based DES at lower molar ratios (<1:2) within the same temperature range [18,19,23,37,60].

A density measurement is vital for many fluid mechanics calculations, mass transfer calculations, and the design of chemical processes. It is possible to use properties derived from density, such as thermal expansion coefficients or compressibility coefficients, to determine the structure of a liquid and its interactions. According to the literature, DESs exhibit higher densities than water and highly depend on temperature. All recorded densities of prepared DES ranged from 1.0849 to 1.0602 g/cm^3 (for comparison, water density is 0.9980 g/cm^3 at room temperature) [35]. A typical range of DES densities reported in the literature [18,19,23,37,58–60] aligned with the experimental findings, showing that DES has a higher density than water. The densities of the precursors also fit within this range. These values lie between the used precursors' room temperature densities (ChCl = 1.1856 g/cm^3 and 1,3 Pdiol = 1.053 g/cm^3). There is good agreement between the density reported in this study (1.0849 g/cm^3) at $T = 298.15$ and those reported by Ozturk and Gonzalez-Miquel [59] (1.08500 g/cm^3), Pandian et al. [58] and (1.08481 g/cm^3) at a molar ratio of 1:2. It is also examined how the molar ratio and temperature affect the density of the solvent. As shown in Fig. S4, densities decrease with increasing temperature. The higher molar ratio (1:2) appears to exhibit higher density compared to the other molar ratios (1:3 to 1:6), as shown in Fig. S2, which was also reported in the literature [19,37,60]. On the other hand, disparities were discernible in the data (1:5 M ratio) submitted by Huang et al., and Gajardo-Parra et al. [19] claimed that no variations with temperature were observed in the measured density at high temperatures ($T > 328.15$ K). Nonetheless, Huang et al.'s [37] data exhibit the temperature dependence behaviour, consistent with our findings.

Knowledge of DES's viscosity may lead to the proper selection of the optimum ratio of HBA and HBD suitable for a particular application and consequently save material and energy. Moreover, this property is vital in designing DESs, as it could influence the hydrodynamic processes in all applications. At room temperature, DESs are liquids, making them easy to handle and suitable for many different applications in industry. Chemical composition, water content, and temperature all influence the viscosity of DES. In general, DES viscosity profiles follow the same trend as that of ILs. At room temperature, the viscosity value of 62.163 mPa.s was the highest. Compared with literature data, this value agrees with that reported by Pandian et al. [58] (67.0 mPa.s) at the same temperature and molar ratio. DESs with high viscosity are not recommended for liquid–liquid extraction, for example. Preheating and pumping requirements will be higher for a viscous DES. A strong hydrogen-bond network may be formed among DES components that account for these high viscosity values, thereby reducing the mobility of organic solutes within the DES matrix. It is possible that other forces, such as electrostatic interactions or van der Waals forces, are also contributing to their high viscosity. As shown in Fig. S5, viscosity values decrease as temperature increases, as interactions between components of DESs weaken. It is clear from this trend that DES is sensitive to thermal fluctuations. Lower viscosities at higher temperatures will likely enhance mass transfer rates in thermally driven processes. As a result of the observed behaviour, it can be concluded that temperature has a notable impact on the rheological properties of DES, and that elevated temperatures reduce cohesive forces within the solvent matrix. Thus, highly viscous DESs cannot be used for practical purposes at ambient conditions but could be considered for technical applications at higher temperatures. As illustrated in Fig. S5, this study supports the findings of Gajardo-Parra et al. [19], where the higher molar ratio (1:3) exhibited greater viscosity than other molar ratios (1:4 to 1:6). On the other hand, viscosity values at the same molar ratio published by Gajardo-Parra et al. [19] and Huang et al. [37] differ marginally. Variations in water contents could be the cause of this.

Knowing the refractive indices of DESs is necessary for determining their possible applications in industrial and chemical processes. As a measure of the electronic polarizability of a medium, RI provides essential information about its identification, purity, and molecular interactions. In Table 1, the refractive indices of prepared DES are reported at varying experimental temperatures. RIs of materials generally decrease with increasing temperature due to reduced polarizability. The investigated DES exhibited higher RI values at $T = 298.15$ K, which changed slightly in all temperatures. Higher RI values were observed for the studied DES at $T = 298.15$ K (for comparison, water RI is 1.3328 at $T = 298.15$ K). Other studies did not investigate the effects of molar ratios on the RI of alkane-diol-based DES.

According to the physicochemical data reported in this study, taking advantage of DES's being less dense and viscous than other well-studied choline-based DESs published in the literature [18,19,23,37,58–60] suggests its suitability for many applications. Depending on the intended application, the advantage of being miscible with water would further enhance its benefit.

4.2. Activity coefficients at infinite dilution and other thermodynamic properties

The infinite dilution activity coefficient values of the 32 solutes were measured using two columns with percentage mass fractions of DES of 27 % and 33 %, respectively, and are listed in Tables S4 and S5. The average values of the two columns are presented in Table 2, and illustrated in Fig. 2 with the temperature ranging from $T = (313.15$ to 343.15 K) at 10 K intervals.

For a given chemical, IDAC values increase with increasing alkyl chain lengths in homologous series for the studied organic solutes in DES. It is observed that when the temperature increases, IDAC decreases for most solutes except for acetonitrile, esters, alkanols, and heterocyclic

Table 2

The experimental average activity coefficients (γ_{13}^{∞}) measured at infinite dilution for selected organic solutes (1) and water in the DES [ChCl +1,3 Pdiol, with the molar ratio of ChCl to 1,3 Pdiol of 1:2] (3) at $T = (313.15, 323.15, 333.15$ and $343.15)$ K. Solute standard states are hypothetical liquids at zero pressure.^a

Solute	T/K			
	313.15	323.15	333.15	343.15
<i>n</i> -hexane	626.0	583.9	520.7	467.8
<i>n</i> -heptane	905.8	860.0	816.7	755.2
<i>n</i> -octane	1067	1022	978.8	955.6
<i>n</i> -nonane	1132	1111	1102	1092
hex-1-ene	333.6	315.9	296.8	272.9
hept-1-ene	531.9	509.5	485.5	467.1
dec-1-ene	1044	1036	1021	1002
hex-1-yne	75.10	73.26	71.88	69.83
hept-1-yne	167.8	162.2	157.2	147.8
oct-1-yne	216.7	213.9	211.1	207.4
cyclopentane	168.2	114.4	90.78	67.75
cyclohexane	258.5	205.3	174.1	138.9
cycloheptane	305.0	248.3	204.5	166.2
cyclooctane	478.2	414.4	341.0	286.7
benzene	26.83	25.56	24.64	23.62
toluene	46.75	46.31	44.96	43.86
ethylbenzene	83.74	81.90	79.82	77.24
<i>m</i> -xylene	90.58	88.15	86.69	85.49
<i>o</i> -xylene	85.04	82.42	80.32	78.10
<i>p</i> -xylene	103.8	99.85	96.38	94.52
acetone	7.225	7.194	7.152	7.121
butan-2-one	12.89	12.74	12.63	12.51
pentan-2-one	21.06	20.98	20.94	20.91
methanol	1.623	1.613	1.604	1.594
ethanol	2.899	2.935	2.979	3.003
propan-1-ol	4.411	4.449	4.528	4.568
propan-2-ol	4.732	4.837	4.973	5.040
methyl acetate	13.20	13.28	13.43	13.54
ethyl acetate	24.43	24.69	25.05	25.34
pyridine	4.048	4.237	4.499	4.670
thiophene	13.08	13.14	13.21	13.28
acetonitrile	0.570	0.598	0.616	0.638
water	4.563	4.493	4.420	4.365

^a Standard uncertainties u (0.68 level of confidence) are $u(p) = 2.0$ kPa, and $u(T) = 0.05$ K and $u(\text{DES mole percent}) = 0.01$. Relative standard uncertainty $u_r(\gamma_{13}^{\infty}) = 8\%$ (for cyclopentane, cyclohexane, *n*-hexane, and hept-1-yne are 59, 38, 16, and 16 %).

compounds. Nonpolar compounds exhibit greater IDAC values than polar compounds at the same temperature. Similar behaviour is also observed for the substituted alkane chains of aromatic hydrocarbons. For instance, ethylbenzene ($\gamma_{13}^{\infty} = 83.739$, at $T = 313.15$ K) has a higher IDAC value (approximately 2-fold) than toluene ($\gamma_{13}^{\infty} = 46.749$, at $T = 313.15$ K). The alkyl chain attached to ethylbenzene makes it more lipophilic, which reduces the affinity between the solute and solvent. The addition of alkyl chains to organic solutes increases their lipophilicity. Alkanes have the highest IDAC values among the 11 organic groups measured. For example, at 313.15 K, the IDAC sequence of the series for the solutes was as follows: alkanes (*n*-nonane, 1131.758) > alkenes (*n*-dec-1-ene, 1044.189) > cycloalkane (cyclooctane, 488.247) > alkynes (oct-1-yne, 216.664) > aromatics (*p*-xylene, 103.788) > esters (ethyl acetate, 24.428) > ketones (propan-2-one, 21.059) > alcohol (propan-2-ol, 4.732) > water (4.563) > heterocyclics (pyridine, 4.048) > nitrile (0.570). This effect can be attributed to the short alkyl chains ($-\text{CH}_2-$) in precursors (HBD and HBA) used in the preparation of DES. The presence of few alkyl chains in both precursors does not allow for the strong van der Waals forces interactions with the alkanes, thus indicating the insolubility of solutes in DES. Additionally, observed lower IDAC values are attributed to organic solutes with higher interaction strengths with DES due to multiple bonding, cyclic or branched structures, or aromatic rings. Water had a low IDAC value ($\gamma_{13}^{\infty} = 0.570$, at $T = 313.15$ K), indicating strong interaction with the DES. This occurred due to the replacement of the homogeneous intramolecular

hydrogen bonding of water molecules with more favourable heterogeneous intramolecular hydrogen bonding between water and DES constituents, causing them to be more soluble in the DES and resulting in longer retention times. Triple bonds exhibit stronger molecular interactions with DES constituents than double bonds. IDAC values for *n*-alkanes are higher than those for their cycloalkane counterparts. The observed behaviour results from molecular packing and spatial accommodation of cyclic structures within the DES matrix, resulting in enhanced van der Waals interactions and improved solute-solvent interactions. Branched chains, cyclisation, and double and triple bonds in organic solutes with the same number of carbon atoms increase their polarity and reduce their IDAC values. As cyclisation, or the double-stranded structure in the solute, results in asymmetrical charge distribution and enhanced polarity, the interaction between the solute and DES will be enhanced. In comparison to alkanes, aromatic compounds have lower IDAC values. Aromatic hydrocarbons exhibit this behaviour due to six delocalised π -electron structures, which cause them to interact strongly with DES. Among xylenes, *o*-xylene has the smallest IDAC value. This phenomenon is caused by the difference in the induced dipole moment on the *o*-xylene molecule and the adjacent methyl groups. Therefore, the constituent molecule deviates from its original position due to intermolecular interactions. Other polar solutes (e.g., esters, ketones, heterocyclics, etc.) have lower IDAC values than alkanes, cycloalkanes, and aromatics, indicating they interact closely with DES. These organic solutes exhibited behaviour due to their organic structures, which are either composed of cation (N^+) or lone pairs of oxygen atoms (O). Alcohols are an example of these interactions, which are seen with low IDAC values in DES. The hydroxyl group (OH) oxygen atom interacted with DES's cation (N^+) because of its two free electrons. Furthermore, the hydroxyl (OH) ions have a high affinity for anions, making OH-containing molecules to be more soluble in DES. Straight-chain alcohols also increase their IDAC values with length, similar to the law of alkanes. Alkyl chains contribute to this effect by enhancing the intermolecular interactions among alcohol molecules. As a result, stronger dipole-dipole forces occur between the alcohols and the DES, leading to decreased dispersive interactions. The molecular structure of ketones and acetonitrile was observed to be affected by the lone pair electrons of oxygen and nitrogen. In ketones, low IDAC values are attributable to hydrogen bonding between the hydroxyl molecules attached to the precursors of DES and the O atoms. Similarly, the nitrogen atom in acetonitrile interacted strongly with the hydroxyls attached to the precursors of DES, where lone pairs are present on the oxygen atoms.

As seen in Table 2, the system temperature strongly influences IDAC values of the investigated solutes. Table 3 presents the calculated thermodynamic properties at infinite dilution at 323.15 K. The IDAC values for most solutes in DES decrease as temperature increases, indicating an endothermic mixing process with poor solubility. A detailed analysis using excess thermodynamic properties is presented later in this section to explain further and support the observed behaviour. Solvation energy and interaction energy between DES and solute could better explain this phenomenon, as the solvation energy was higher than the interaction energy. This is due to weaker molecular interactions between solutes and DESs than between solute and solute. Conversely, alkanols, esters, water, and heterocyclics showed $\Delta H_i^{\text{E},\infty}$ values lower than zero, consistent with their increasing IDAC values as temperature increases. In these solutes, the $\Delta H_i^{\text{E},\infty}$ values are negative, which indicates that the molecules in the solute intermolecularly interact strongly with those of the DES. It is evident from this that these solutes and DES deviate from Raoult's law negatively. In the DES matrix, the observed negative values indicate the exothermic nature of the mixing process, which indicates favourable solute-solvent interactions. According to Table 3, all organic solutes except cyclopentane, cyclohexane, and cycloheptane have negative $T_{\text{ref}}\Delta S_i^{\text{E},\infty}$ values. In this regard, the observed behaviour suggests an increase in molecular ordering relative to an ideal solution,

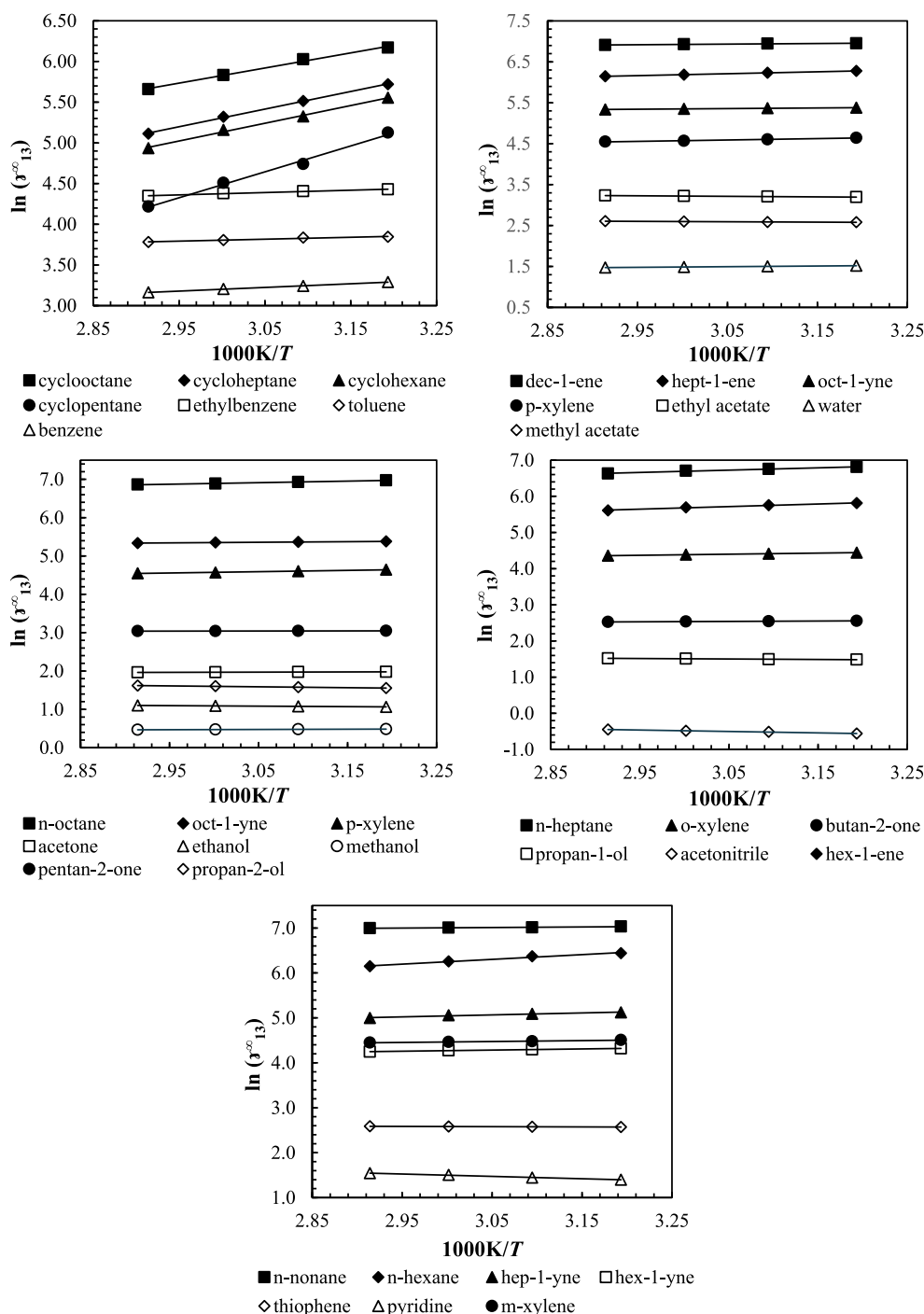


Fig. 2. The plots of $\ln(\gamma_{13}^{\infty})$ values for selected organic solutes in DES (3) investigated at 101.3 ± 2 kPa and varying temperatures.

likely due to a reduction in the number of independent kinetic units caused by the net formation of hydrogen bonds.

The $\Delta G_i^{E,\infty}$ value of water is less than zero; those of the other solutes are greater than zero. This indicates that the dissolution of water in DES is more favourable than ideal mixing when the $\Delta G_i^{E,\infty}$ is negative. In contrast, positive values suggest that mixing may remain favourable, though to a lesser extent than in the ideal scenario. The $\Delta G_i^{E,\infty}$ values increase with carbon atoms for linear alkanes, corresponding to the IDAC data. The $\Delta G_i^{E,\infty}$ value of *n*-nonane is the highest (18.259 kJ/mol), and the value of water (-1.338 kJ/mol) is the lowest among all solutes at $T_{\text{ref}} = 323.15$ K. For *n*-alkanes, $\Delta G_i^{E,\infty}$ values are higher, meaning the

interaction between the solutes and DES is weaker. With water, a polar solute with lone pairs of O atoms forms strong hydrogen bonds with solvents (i.e., DESs and ILs) due to delocalised electrons and polar groups.

Table 4 lists the K_L values of all solutes at corresponding temperatures. It was evident that K_L followed a similar trend to γ_{13}^{∞} . Components with high K_L values indicate that their concentration in the stationary phase is large, and they have a long retention time. An opposite situation occurs when K_L is small. In all cases, K_L values decreased with increasing temperature. Compared to other solutes, *n*-alkanes have a lower K_L value, which indicates low solubility in the DES. Observed behaviour occurs because solutes volatilise more easily at higher temperatures,

Table 3

Coefficients a and b of Eq. (8), limiting partial molar excess enthalpies ($\Delta H_i^{E,\infty}$), entropies ($T_{ref}\Delta S_i^{E,\infty}$), and Gibbs free energies ($\Delta G_i^{E,\infty}$) for organic solutes in DES [ChCl +1,3 Pdiol, with the molar ratio of ChCl to 1,3 Pdiol of 1:2] at a reference temperature $T = 323.15$ K and $p = (101.3 \pm 2)$ kPa.^a

Solute	a	b	$\Delta H_i^{E,\infty}$	$T_{ref}\Delta S_i^{E,\infty}$	$\Delta G_i^{E,\infty}$
		K	kJ.mol^{-1}	kJ.mol^{-1}	kJ.mol^{-1}
<i>n</i> -hexane	1.06	3.07	8.81	−7.78	16.6
<i>n</i> -heptane	0.64	4.77	5.32	−12.3	17.6
<i>n</i> -octane	0.41	5.68	3.36	−14.7	18.0
<i>n</i> -nonane	0.12	6.64	1.03	−17.2	18.3
hex-1-ene	0.71	3.54	5.93	−9.06	15.0
hept-1-ene	0.47	4.77	3.91	−12.3	16.2
dec-1-ene	0.15	6.48	1.23	−16.8	18.1
hex-1-yne	0.25	3.51	2.12	−9.06	11.2
oct-1-yne	0.16	3.73	1.29	−12.7	14.0
cyclopentane	3.18	4.89	26.5	14.1	12.3
cyclohexane	2.18	−1.40	18.10	4.24	13.9
cycloheptane	2.17	−5.06	18.0	3.64	14.4
cyclooctane	1.86	−1.19	15.4	−0.26	15.7
benzene	0.45	1.85	3.75	−4.69	8.44
toluene	0.24	3.10	1.96	−8.02	9.99
ethylbenzene	0.29	3.51	2.39	−9.08	11.5
<i>m</i> -xylene	0.21	3.85	1.70	−9.96	11.7
<i>o</i> -xylene	0.30	3.48	2.51	−8.97	11.5
<i>p</i> -xylene	0.34	3.55	2.83	−9.16	12.0
acetone	0.05	1.81	0.44	−4.70	5.14
butan-2-one	0.11	2.22	0.87	−5.75	6.63
pentan-2-one	0.03	2.97	0.21	−7.71	7.92
methanol	0.06	0.28	0.52	−0.72	1.25
ethanol	−0.13	1.48	−1.07	−3.88	2.80
propan-1-ol	−0.13	1.90	−1.10	−4.98	3.89
propan-2-ol	−0.23	2.30	−1.94	−6.05	4.10
methyl acetate	−0.10	2.88	−0.79	−7.52	6.73
ethyl acetate	−0.13	3.62	−1.11	−9.46	8.35
thiophene	−0.06	2.75	−0.46	−7.17	6.71
pyridine	−0.53	3.08	−4.37	−8.14	3.76
acetonitrile	0.16	1.01	1.34	−2.58	3.91
water	−0.40	0.70	−3.29	−1.95	−1.34

^a Standard uncertainties u (0.68 level of confidence) are $u(p) = 2.0$ kPa, $u(T) = 0.05$ K, $u(\text{DES mole percent}) = 0.01$ and $u(\Delta H_i^{E,\infty}, \Delta G_i^{E,\infty}, T_{ref}\Delta S_i^{E,\infty}) = 0.05$ kJ/mol. Relative standard uncertainty $u_r(\gamma_{13}^\infty) = 8\%$ (for cyclopentane, cyclohexane, *n*-hexane, and hept-1-yne are 59, 38, 16, and 16 %).

resulting in lower K_L values. Compared with nonpolar solutes, polar solutes displayed higher K_L values, as DES-charged particles formed stronger electrostatic and hydrogen-bonding interactions with them. In this case, solute symmetry affects the polarity of the solute. Symmetric solute structure has a lower polarity and a smaller K_L value. Propan-2-ol had the highest K_L value (413.946) at 313.15 K, whereas *n*-hexane had the lowest (1.305). Propan-2-ol has poor symmetry and higher polarity, which makes it highly soluble and has a high K_L value in DES, owing to the asymmetry of its structure. A strong interaction between polar molecules and DES underscores the greater relevance of K_L values in polar solutes compared to nonpolar solutes. In both *n*-alkanes and straight-chain alcohols, as long as their structures are similar, their K_L values increase with the carbon number. Introducing double-bonded or ring structures increases the K_L values of organic solutes with the same number of carbon atoms. Solute and DES interact better when this group (i.e., double-bonded or ring) is present.

4.3. Evaluation of DES separation potential on industrial mixtures

Selectivity ($S_{ij}^\infty = \gamma_i^\infty/\gamma_j^\infty$) and capacity ($k_j^\infty = 1/\gamma_j^\infty$) at infinite dilution are among the most important parameters for designing an effective extraction process involving binary azeotropic or near-azeotropic, close-boiling mixtures. Specifically, S_{ij}^∞ measures solvent separation ability, whereas k_j^∞ measures solvent dissolution ability. A high S_{ij}^∞ value corresponds to a low investment cost. k_j^∞ measures the

Table 4

The experimental (gas–liquid) partition coefficients K_L for the solutes and water (1) in DES [ChCl +1,3 Pdiol, with the molar ratio of ChCl to 1,3 Pdiol of 1:2] (3) at $T = (313.15, 323.15, 333.15 \text{ and } 343.15)$ K and $p = (101.3 \pm 2)$ kPa.^a

Solute	T/K			
	313.15	323.15	333.15	343.15
<i>n</i> -hexane	1.305	0.992	0.813	0.681
<i>n</i> -heptane	2.692	1.905	1.390	1.070
<i>n</i> -octane	6.452	4.316	2.989	2.094
<i>n</i> -nonane	16.83	10.50	6.718	4.448
hex-1-ene	2.018	1.540	1.215	1.003
hept-1-ene	3.711	2.651	1.958	1.470
dec-1-ene	44.12	25.68	15.69	9.986
hex-1-yne	11.93	8.527	6.213	4.679
oct-1-yne	15.23	10.59	7.595	5.752
cyclopentane	33.87	21.75	14.47	9.994
cyclohexane	1.556	1.510	1.319	1.319
cycloheptane	7.532	7.701	6.934	6.799
cyclooctane	16.19	13.08	10.77	9.254
benzene	35.16	24.73	18.99	14.79
toluene	50.30	35.53	25.61	19.14
ethylbenzene	79.16	53.10	37.47	27.01
<i>m</i> -xylene	117.4	76.47	51.60	36.12
<i>o</i> -xylene	126.7	82.04	54.37	37.08
<i>p</i> -xylene	169.5	112.9	71.81	51.01
acetone	107.6	73.02	47.47	33.85
butan-2-one	72.93	52.14	38.27	28.69
pentan-2-one	99.50	68.74	48.73	35.47
methanol	131.5	88.48	61.12	43.29
ethanol	260.8	163.7	106.0	70.50
propan-1-ol	253.9	166.9	113.1	78.14
propan-2-ol	413.9	248.8	154.3	98.99
methyl acetate	196.0	119.4	74.96	48.82
ethyl acetate	41.60	29.25	21.01	15.53
thiophene	48.01	32.50	22.56	16.15
pyridine	110.7	75.52	53.01	38.22
acetonitrile	1202	743.4	468.0	310.6
water	285.3	200.4	144.5	106.2

^a Standard uncertainties u (0.68 level of confidence) are $u(p) = 2.0$ kPa, $u(T) = 0.05$ K and $u(\text{DES mole percent}) = 0.01$. Relative standard uncertainty $u_r(\gamma_{13}^\infty) = 8\%$ (for cyclopentane, cyclohexane, *n*-hexane, and hept-1-yne are 59, 38, 16, and 16 %), and $u_r(K_L) = 5\%$.

amount of extractant used in a separation process. Significant differences in the activity coefficient at infinite dilution values must be present if the components are to be separated. The typical separation problems selected were mixtures of aliphatics – aromatics (represented by heptane – benzene mixture), desulphurisation of liquid fuel (represented by heptane – thiophene mixture), oxygenation additive (hexane – ethanol), ethyl propionate raw material (cyclohexane – ethanol) and octane – acetonitrile. S_{ij}^∞ and k_j^∞ for selected industrial separation problems are shown in Table 5 at $T = 323.15$ K. In the chemical industry, aliphatic and aromatic hydrocarbon separation is crucial. DES examined in this study reveals the highest value of S_{ij}^∞ . This value is twice that of TPABr +1,6 Hdiol (10.4), and three times higher than that of TMAcI +1,6 Hdiol (7.3) and ChCl +1,5 Pdiol (6.6) [29,61,62]. The results of this current study indicate that DES can be used as a highly effective selective solvent for separating substances with large polarity differences. A comparison of the k_j^∞ for benzene (0.04) at $T = 323.15$ K for the same separation problem is much higher than the value reported for ChCl +1,5 Pdiol (0.03) [29], but much lower than for 1,6 Hdiol (0.20) [32]. The amount of DES required for extraction would be large, resulting in a higher energy requirement for solvent extraction and solvent recovery. Fuel desulphurisation is another critical issue. In the heptane/thiophene extraction process, the investigated DES has a slightly higher S_{ij}^∞ (44.4), which is on an average level. Comparing the S_{ij}^∞ values of DES obtained in this work with those reported earlier, it is found that the S_{ij}^∞ of heptane/thiophene is four times lower than the S_{ij}^∞ for TPABr +1,6 Hdiol (173.6) [61]. The second and third best are also

Table 5Selectivities (S_{ij}^{∞}) and capacities (k_j^{∞}) at infinite dilution for several alkane-diol DESs at $T = 323.15$ K and $p = (101.3 \pm 2)$ kPa.^a

Solvent	$S_{ij}^{\infty} / k_j^{\infty}$						
	<i>n</i> -hexane/ benzene	<i>n</i> -hexane/ ethanol	<i>n</i> -heptane/ thiophene	<i>n</i> -octane/ acetonitrile	cyclohexane/ ethanol		Reference
ChCl +1,3 Pdiol; [1:2]	22.8/0.04	198.9/0.34	44.4/0.08	1709.2/1.67	70.0/0.34		This work
EMPYR-Br + 1,5 Pdiol; [1:2]	2.3/0.77	–	–	–	8.7/3.33		[63]
1,6 Hdiol	4.3/0.20	20.6/0.95	64.9/2.18	9.86/0.25	12.7/0.95		[32]
TMAcI +1,6 Hdiol; [1:1]	7.33/0.10	40.8/0.58	90.8/1.29	–	20.6/0.58		[62]
EMPYR-Br + 1,6 Hdiol; [1:2]	1.9/0.61	2.6/0.84	–	–	2.0/0.84		[64]
ChCl +1,5 Pdiol; [1:4]	6.6/0.03	102.5/0.49	18.6/0.08	–	94.6/0.49		[29]
TPABr +1,6 Hdiol; [1:2]	10.42/0.49	40.9/1.92	173.85/6.13	–	21.2/1.92		[61]

ChCl +1,3 Pdiol: Choline chloride +1,3 Propanediol.

{EMPYR-Br + 1,5 Pdiol: 1-ethyl-1-methylpyrrolidinium bromide +1,5 Pentanediol}.

{1,6 Hdiol: 1,6 Hexanediol}.

{EMPYR-Br + 1,6 Hdiol: 1-ethyl-1-methylpyrrolidinium bromide +1,6 Hexanediol}.

{ChCl +1,5 Pdiol: Choline chloride +1,5 Pentanediol}.

{TPABr +1,6 Hdiol: Tetrapropylammonium bromide +1,6 Hexanediol}.

{TMAcI +1,6 Hdiol: Tetramethylammonium chloride +1,6 Hexanediol}.

^a Standard uncertainties u are $u(p) = 2.0$ kPa, $u(T) = 0.05$ K and $u(\text{DES mole percent}) = 0.01$.

those for TMAcI +1,6 Hdiol (90.8) and 1,6 Hdiol (64.9). Despite the DES's ease of separation capability for the heptane/thiophene system, its k_j^{∞} (0.08) is very low compared to that of TMAcI +1,6 Hdiol (1.29) [62]. Another interesting separation problem is the extraction of acetonitrile from octane, which holds significant relevance for a number of manufacturing industries, such as solvent recycling, solvent recovery, fine chemical synthesis, dye synthesis, and polymer synthesis. The highest value of S_{ij}^{∞} has been measured for the tested DES (1709.2). The k_j^{∞} value is higher (1.67) than that for 1,6 Hdiol (0.25) [32], indicating a lower amount of DES required as an extraction solvent. DES was further investigated as a designer solvent for extracting ethanol from hexane and cyclohexane in this study, which forms a minimum boiling azeotrope with a mixture that deviates significantly from the ideal liquid phase behaviour of the solution. Among its uses in the petrochemical industry, extracted ethanol is an oxygenating additive to gasoline and a base for the manufacture of ethyl propionate. Investigated DES reveals promising results. The S_{ij}^{∞} value for ethanol extraction from hexane (198.9) is higher than that of ChCl +1,5 Pdiol (102.5) [29]. Contrastingly, ethanol is extracted from cyclohexane (70.0) with greater efficiency but less than ChCl +1,5 Pdiol (94.6) [29]. Despite their attractive S_{ij}^{∞} values, they are hampered by their poor k_j^{∞} (0.34 and 0.49). This finding indicates that DES does not require as many equilibrium stages as other solvents for separating these selected components.

Conversely, to support this claim, a more in-depth experimental investigation (liquid–liquid or vapour–liquid equilibrium) should be conducted to assess solvent extraction capabilities at various solvent feed ratios and feed concentrations for the observed promising separation problems. In this way, it will be possible to determine whether or not DES is a feasible alternative solvent. Since density and viscosity are DES-related issues, it is possible to understand their effects in these measurements.

5. Conclusion

The molecular interaction between [ChCl +1,3 Pdiol] DES and 32 polar and nonpolar organic solutes was investigated using gas-liquid chromatography at a wide temperature range from $T = (313.15$ to $343.15)$ K. It can be concluded from the results that the strength of the (solute + solvent) interactions strongly depends on the alkyl chain length and chain branching degree in the dissolved substance. Heteroatoms increase the compound's polarity, resulting in lower values of γ_{13}^{∞} when present in the solute molecule. Partial molar excess thermodynamic functions and the gas-liquid partition coefficients at infinite dilution further explained the interaction patterns between DES and organic solutes. A physicochemical analysis of DES was conducted prior

to its assessment to determine its nature as an extractant.

S_{ij}^{∞} and k_j^{∞} at infinite dilution, for common industrial separation problems, were calculated using the activity coefficients. The S_{ij}^{∞} values for selected separation problems are quite high compared to other DESs reported in this work. Comparing the selectivity values of DES obtained in this work with those obtained previously for many diol-based DESs and industrial solvents shows a substantial and optimistic separation efficiency for these problems.

CRediT authorship contribution statement

Banzi P. Mbatha: Writing – original draft, Methodology, Investigation, Formal analysis. **Peterson T. Ngema:** Writing – review & editing, Supervision, Resources. **Suresh Ramsuroop:** Writing – review & editing, Supervision, Resources. **Kaniki Tumba:** Writing – review & editing, Resources. **Lindokuhle Manyoni:** Writing – review & editing, Validation, Data curation. **Nkululeko Nkosi:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Nkululeko Nkosi reports financial support was provided by National Research Foundation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study has been supported by the Durban University of technology, Mangosuthu University of Technology and National Research Foundation (Grant No: TTK23032988051) in South Africa. Author B. Mbatha wishes to thank Mrs. N.P. Cele (DUT-Chemistry), Dr. V. Mzozoyana (UKZN-Chemistry) and Mrs. N.M. Xhakaza (DUT-Chemistry) for their assistance with sample analysis and characterisation.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2025.128320>.

Data availability

No data was used for the research described in the article.

References

- [1] A. Saha, S. Bhattacharjee, Research and review: based on distillation, distillation types and advancements: a short summary, *J. Adv. Pharm. Pract.* 1 (2019) 8–16, <https://doi.org/10.5281/zenodo.2545018>.
- [2] A. Bokhary, M. Leitch, B.Q. Liao, Liquid–liquid extraction technology for resource recovery: applications, potential, and perspectives, *J. Water Process Eng* 40 (2021) 101762, <https://doi.org/10.1016/j.jwpe.2020.101762>.
- [3] M. Neubauer, T. Wallek, S. Lux, Deep eutectic solvents as entrainers in extractive distillation – a review, *Chem. Eng. Res. Des.* 184 (2022) 402–418, <https://doi.org/10.1016/j.cherd.2022.06.019>.
- [4] C.F. Poole, Milestones in the development of liquid-phase extraction techniques, in: *Liq. Extr.*, Elsevier, 2020, pp. 1–44, <https://doi.org/10.1016/B978-0-12-816911-7.00001-3>.
- [5] X. Zhou, X. Zhou, C. Wang, H. Zhou, Environmental and human health impacts of volatile organic compounds: a perspective review, *Chemosphere* 313 (2023) 137489, <https://doi.org/10.1016/j.chemosphere.2022.137489>.
- [6] A.C. Lewis, J.R. Hopkins, D.C. Carslaw, J.F. Hamilton, B.S. Nelson, G. Stewart, J. Dornie, N. Passant, T. Murrells, An increasing role for solvent emissions and implications for future measurements of volatile organic compounds, *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* 378 (2020) 20190328, <https://doi.org/10.1098/rsta.2019.0328>.
- [7] W.H. Organization, others, WHO global air quality guidelines: particulate matter (PM_{2.5} and PM₁₀), ozone, nitrogen dioxide, sulfur dioxide and carbon monoxide: executive summary, in: *WHO Glob. Air Qual. Guidel. Part. Matter (PM_{2.5} PM₁₀), Ozone, nitrogen dioxide, Sulfur dioxide carbon monoxide Exec. Summ.*, 2021.
- [8] R. Malolan, K.P. Gopinath, D.V.N. Vo, R.S. Jayaraman, S. Adithya, P.S. Ajay, J. Arun, Green ionic liquids and deep eutectic solvents for desulphurization, denitrification, biomass, biodiesel, bioethanol and hydrogen fuels: a review, *Environ. Chem. Lett.* 192 (2020) 1001–1023, <https://doi.org/10.1007/S10311-020-01113-7>.
- [9] J. Plotka-Wasyłka, M. De La Guardia, V. Andrich, M. Vilková, Deep eutectic solvents vs ionic liquids: Similarities and differences, *Microchem. J.* 159 (2020) 105539, <https://doi.org/10.1016/j.microc.2020.105539>.
- [10] F.M. Perna, P. Vitale, V. Capriati, Deep eutectic solvents and their applications as green solvents, *Curr. Opin. Green Sustain. Chem.* 21 (2020) 27–33, <https://doi.org/10.1016/j.cogsc.2019.09.004>.
- [11] Á. Santana-Mayor, R. Rodríguez-Ramos, A.V. Herrera-Herrera, B. Socas-Rodríguez, M.Á. Rodríguez-Delgado, Deep eutectic solvents. The new generation of green solvents in analytical chemistry, *TrAC Trends Anal. Chem.* 134 (2021) 116108, <https://doi.org/10.1016/j.trac.2020.116108>.
- [12] S.K. Singh, A.W. Savoy, Ionic liquids synthesis and applications: an overview, *J. Mol. Liq.* 297 (2020) 112038, <https://doi.org/10.1016/j.molliq.2019.112038>.
- [13] G. Kaur, H. Kumar, M. Singla, Diverse applications of ionic liquids: a comprehensive review, *J. Mol. Liq.* 351 (2022) 118556, <https://doi.org/10.1016/j.molliq.2022.118556>.
- [14] C.-W. Cho, T.P.T. Pham, Y. Zhao, S. Stolte, Y.-S. Yun, Review of the toxic effects of ionic liquids, *Sci. Total Environ.* 786 (2021) 147309, <https://doi.org/10.1016/j.scitotenv.2021.147309>.
- [15] N. Winterton, The green solvent: a critical perspective, *Clean Technol. Environ. Policy* 239 (23) (2021) 2499–2522, <https://doi.org/10.1007/S10098-021-02188-8>.
- [16] S.S. de Jesus, R. Maciel Filho, Are ionic liquids eco-friendly? *Renew. Sustain. Energy Rev.* 157 (2022) 112039, <https://doi.org/10.1016/j.rser.2021.112039>.
- [17] S. Magina, A. Barros-Timmons, S.P.M. Ventura, D.V. Evtuguin, Evaluating the hazardous impact of ionic liquids – challenges and opportunities, *J. Hazard. Mater.* 412 (2021) 125215, <https://doi.org/10.1016/j.jhazmat.2021.125215>.
- [18] V.P. Cotroneo-Figueroa, N.F. Gajardo-Parra, P. López-Portfiri, Á. Leiva, M. Gonzalez-Miquel, J.M. Garrido, R.I. Canales, Hydrogen bond donor and alcohol chain length effect on the physicochemical properties of choline chloride based deep eutectic solvents mixed with alcohols, *J. Mol. Liq.* 345 (2022) 116986, <https://doi.org/10.1016/j.molliq.2021.116986>.
- [19] N.F. Gajardo-Parra, V.P. Cotroneo-Figueroa, P. Aravena, V. Vesovic, R.I. Canales, Viscosity of choline chloride-based deep eutectic solvents: experiments and modeling, *J. Chem. Eng. Data* 65 (2020) 5581–5592, <https://doi.org/10.1021/acs.jced.0c00715>.
- [20] K. Biernacki, H.K.S. Souza, C.M.R. Almeida, A.L. Magalhães, M.P. Gonçalves, Physicochemical properties of choline chloride-based deep eutectic solvents with polyols: an experimental and theoretical investigation, *ACS Sustain. Chem. Eng.* 8 (2020) 18712–18728, <https://doi.org/10.1021/acssuschemeng.0c08288>.
- [21] H.S. Esfahani, A. Khoshshima, G. Pazuki, A. Hosseini, Separation of methanol and ethanol from azeotropic MTBE mixtures using choline chloride-based deep eutectic solvents, *J. Mol. Liq.* 381 (2023) 121641, <https://doi.org/10.1016/j.molliq.2023.121641>.
- [22] W. Dou, J. Yu, X. Wang, Effect of ethanol on the density and viscosity of choline chloride/urea eutectic system, *J. Mol. Liq.* 382 (2023) 121923, <https://doi.org/10.1016/j.molliq.2023.121923>.
- [23] P. Han, W. Nie, G. Zhao, P. Gao, Theoretical investigation on the structure and physicochemical properties of choline chloride-based deep eutectic solvents, *J. Mol. Liq.* 366 (2022) 120243, <https://doi.org/10.1016/j.molliq.2022.120243>.
- [24] A. Ghanadzadeh Gilani, B. Mohammadi Khanghah, J. Jahanbin Sardroodi, G. Pazuki, Liquid–liquid equilibria for binary azeotropic mixtures of heptane and amyl alcohols using different choline chloride based deep eutectic solvents at 298.15 K, *Ind. Eng. Chem. Res.* 61 (2022) 4068–4082, <https://doi.org/10.1021/acs.iecr.1c04610>.
- [25] H.J. Hayler, S. Perkin, The eutectic point in choline chloride and ethylene glycol mixtures, *Chem. Commun.* 58 (2022) 12728–12731, <https://doi.org/10.1039/D2CC04008E>.
- [26] E.J. Sa, B.S. Lee, B.H. Park, Separation of *n*-hexane-ethanol azeotropic mixture using choline chloride +1,4-butanediol deep eutectic solvents, *Chem. Eng. Res. Des.* 192 (2023) 1–11, <https://doi.org/10.1016/j.cherd.2023.02.011>.
- [27] N. Mgxadeni, B. Kabane, I. Bahadur, R.S. Varma, S.K. Singh, Deep eutectic solvents as sustainable solvents for industrial separation problems: a recent update, *J. Ion. Liq.* 3 (2023) 100065, <https://doi.org/10.1016/j.jil.2023.100065>.
- [28] L.P. Silva, M.A.R. Martins, J.H.F. Conceição, S.P. Pinho, J.A.P. Coutinho, Eutectic mixtures based on polyalcohols as sustainable solvents: screening and characterization, *ACS Sustain. Chem. Eng.* 8 (2020) 15317–15326, <https://doi.org/10.1021/acssuschemeng.0c05518>.
- [29] Y. Li, W. Wang, Q. Wang, N. Yalikun, J. Tang, Thermodynamic parameters and infinite dilution activity coefficients for organic solutes in deep eutectic solvent: choline chloride + 1,5-pentanediol, *J. Chem. Thermodyn.* 170 (2022) 106784, <https://doi.org/10.1016/j.jct.2022.106784>.
- [30] N. Nkosi, K. Tumba, S. Ramsuroop, Measurements of activity coefficient at infinite dilution for organic solutes in tetramethylammonium chloride + ethylene glycol deep eutectic solvent using gas-liquid chromatography, *Fluid Phase Equilib.* 462 (2018) 31–37, <https://doi.org/10.1016/j.fluid.2018.01.019>.
- [31] B.P. Mbatha, P.T. Ngema, N. Nkosi, S. Ramsuroop, Infinite dilution activity coefficient measurements for 1-methyl-4-(1-methylethenyl)-cyclohexene as a green solvent for separation, *J. Chem. Eng. Data* 67 (2022) 966–974, <https://doi.org/10.1021/acs.jced.1c00801>.
- [32] N. Nkosi, K. Tumba, P. Ngema, S. Ramsuroop, Infinite dilution activity coefficients and thermodynamic properties of selected organic solutes and water dissolved in 1, 6-hexanediol, *J. Chem. Thermodyn.* 151 (2020) 106163, <https://doi.org/10.1016/j.jct.2020.106163>.
- [33] J. Kestin, M. Sokolov, W.A. Wakeham, Viscosity of liquid water in the range –8 °C to 150 °C, *J. Phys. Chem. Ref. Data Monogr.* 7 (1978) 941–948, <https://doi.org/10.1063/1.555581>.
- [34] M.L. Huber, R.A. Perkins, A. Laesecke, D.G. Friend, J.V. Sengers, M.J. Assael, I. N. Metaxa, E. Vogel, R. Mareš, K. Miyagawa, New international formulation for the viscosity of H₂O, *J. Phys. Chem. Ref. Data Monogr.* 38 (2009) 101–125, <https://doi.org/10.1063/1.3088050>.
- [35] W. Wagner, A. Pruß, The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use, *J. Phys. Chem. Ref. Data* 31 (2002) 387–535, <https://doi.org/10.1063/1.1461829>.
- [36] A.H. Harvey, J.S. Gallagher, J.M.H.L. Sengers, Revised formulation for the refractive index of water and steam as a function of wavelength, temperature and density, *J. Phys. Chem. Ref. Data* 27 (1998) 761–774, <https://doi.org/10.1063/1.556029>.
- [37] J.Y. Huang, W.J. Jiang, P. Xiao, Z.T. Fan, F.Y. Zhong, H.L. Peng, J. Du, K. Huang, Physical properties and NH₃ solubilities of deep eutectic solvents formed by choline chloride and glycols, *Fluid Phase Equilib.* 529 (2021) 112871, <https://doi.org/10.1016/j.fluid.2020.112871>.
- [38] A.C. Baelhadj, F. Mutelet, B. Jiang, W.E. Acree, Activity coefficients at infinite dilution for organic solutes dissolved in two 1,2,3-tris(diethylamino)cyclopentylm based room temperature ionic liquids, *J. Mol. Liq.* 223 (2016) 89–99, <https://doi.org/10.1016/j.molliq.2016.08.028>.
- [39] C.F. Chien, M.M. Kopećni, R.J. Laub, C.A. Smith, Solute liquid-gas activity and partition coefficients with mixtures of *n*-hexadecane and *n*-octadecane with *N,N*-dibutyl-2-ethylhexylamide solvents, *J. Phys. Chem.* 85 (1981) 1864–1871, <https://doi.org/10.1021/j150613a018>.
- [40] B.W. Gainey, C.L. Young, Activity coefficients of benzene in solution of *n*-alkanes and the second virial coefficients of benzene + nitrogen mixtures. Gas-chromatographic investigation, *Trans. Faraday Soc.* 64 (1968) 349, <https://doi.org/10.1039/tf9686400349>.
- [41] R.C. Castells, E.L. Arancibia, A.M. Nardillo, C. Castells, Thermodynamics of hydrocarbon solutions using g.l.c. *n*-hexane, *n*-heptane, benzene, and toluene as solutes each at infinite dilution in *n*-hexadecane, in *n*-octadecane, and in *n*-eicosane, *J. Chem. Thermodyn.* 22 (1990) 969–977, [https://doi.org/10.1016/0021-9614\(90\)90186-T](https://doi.org/10.1016/0021-9614(90)90186-T).
- [42] Y. Iwai, M. Yamashita, K. Kohashi, Y. Arai, Measurement and prediction of infinite dilution activity coefficients for C₆ hydrocarbons in heavy paraffinic hydrocarbons, *Kagaku Kogaku Ronbunshu* 14 (1988), <https://doi.org/10.1252/kakoronbunshu.14.706>.
- [43] T.M. Letcher, P. Jerman, Activity coefficients of cyclohexane + *n*-alkane mixtures, *J. Chem. Thermodyn.* 8 (1976) 127–131, [https://doi.org/10.1016/0021-9614\(76\)90085-9](https://doi.org/10.1016/0021-9614(76)90085-9).
- [44] P.S. Snyder, J.F. Thomas, Solute activity coefficients at infinite dilution via gas–liquid chromatography, *J. Chem. Eng. Data* 13 (1968) 527–529, <https://doi.org/10.1021/jc60039a021>.
- [45] C.P. Hicks, C.L. Young, Activity coefficients of C₄–C₈ *n*-alkanes in C₁₆–C₃₂ *n*-alkanes, *Trans. Faraday Soc.* 64 (1968) 2675–2682, <https://doi.org/10.1039/tf9686402675>.
- [46] D.H. Everett, Effect of gas imperfection on G.L.C. Measurements : a refined method for determining activity coefficients and second virial coefficients, *Trans. Faraday Soc.* 61 (1965) 1637, <https://doi.org/10.1039/tf9656101637>.
- [47] B.E. Poling, J.M. Prausnitz, J.P. O'Connell, The properties of gases & liquids, 2001, [https://doi.org/10.1016/0894-1777\(88\)90021-0](https://doi.org/10.1016/0894-1777(88)90021-0).
- [48] D.R. Lide, CRC handbook of chemistry and physics, in: 2003–2004, *Handb. Chem. Phys.*, 84th edition, 2003, <https://doi.org/10.1136/oem.53.7.504>.
- [49] A.J.B. Cruickshank, M.L. Windsor, C.L. Young, The use of gas-liquid chromatography to determine activity coefficients and second virial coefficients of

- mixtures. I. Theory and verification of method of data analysis, *Proc. R. Soc. A Math. Phys. Eng. Sci.* 295 (1966) 259–270, <https://doi.org/10.1098/rspa.1966.0239>.
- [50] M. McGlashan, D. Potter, An apparatus for the measurement of the second virial coefficients of vapours; the second virial coefficients of some *n*-alkanes and some mixtures of *n*-alkanes, *Proc. R. Soc. Lond. A.* 267 (1962) 478–500, <https://doi.org/10.1098/rspa.1962.0114>.
- [51] T.M. Letcher, Activity coefficients at infinite dilution from gas-liquid chromatography, *Faraday Symp. Chem. Soc.* 15 (1980) 103–112, <https://doi.org/10.1039/FS9801500103>.
- [52] J.M. Smith, V.H.C. Ness, M.M. Abbot, *Introduction to chemical engineering thermodynamics*, 2000.
- [53] R. Costa, A.T.S.C. Brandão, C.M. Pereira, A.F. Silva, Electrified interfaces of deep eutectic solvents, *Electrochim. Acta* 461 (2023) 142653, <https://doi.org/10.1016/J.ELECTACTA.2023.142653>.
- [54] C. Wu, Y. Han, H. Zhao, C. Zheng, X. Li, J. Ni, Effect of choline chloride/multiple diols deep eutectic solvents on the friction and vibration performance of Si₃N₄/GCr₁₅ hybrid ceramic ball bearings, *Tribol. Int.* 198 (2024) 109845, <https://doi.org/10.1016/J.TRIBOINT.2024.109845>.
- [55] H. Wang, S. Liu, Y. Zhao, J. Wang, Z. Yu, Insights into the hydrogen bond interactions in deep eutectic solvents composed of choline chloride and polyols, *ACS Sustain. Chem. Eng.* 7 (8) (2019) 7760–7767, <https://doi.org/10.1021/ACSSUSCHEMENG.8B06676>.
- [56] J. Yue, Z. Zhu, J. Yi, H. Li, B. Chen, J. Rao, One-step extraction of oat protein by choline chloride-alcohol deep eutectic solvents: role of chain length of dihydric alcohol, *Food Chem.* 376 (2022) 131943, <https://doi.org/10.1016/j.foodchem.2021.131943>.
- [57] W. Yu, Y. Bo, Y. Luo, X. Huang, R. Zhang, J. Zhang, Enhancing effect of choline chloride-based deep eutectic solvents with polyols on the aqueous solubility of curcumin—insight from experiment and theoretical calculation, *Chin. J. Chem. Eng.* 59 (2023) 160–168, <https://doi.org/10.1016/J.CJCHE.2023.01.005>.
- [58] R. Pandian, D. Kim, Y. Zhang, I. Alfurayj, D.M. Prado, E. Maginn, C. Burda, Chain length and OH-spacing effects on diol-based deep eutectic solvents, *J. Mol. Liq.* 393 (2024) 123534, <https://doi.org/10.1016/j.molliq.2023.123534>.
- [59] B. Ozturk, M. Gonzalez-Miquel, Alkanediol-based deep eutectic solvents for isolation of terpenoids from citrus essential oil: experimental evaluation and COSMO-RS studies, *Sep. Purif. Technol.* 227 (2019) 115707, <https://doi.org/10.1016/J.SEPPUR.2019.115707>.
- [60] X. Deng, X. Duan, L. Gong, D. Deng, Ammonia solubility, density, and viscosity of choline chloride-dihydric alcohol deep eutectic solvents, *J. Chem. Eng. Data* 65 (2020) 4845–4854, <https://doi.org/10.1021/acs.jced.0c00386>.
- [61] N. Nkosi, K. Tumba, S. Ramsuroop, Activity coefficients at infinite dilution of various solutes in tetrapropylammonium bromide + 1,6-hexanediol deep eutectic solvent, *J. Chem. Eng. Data* 63 (2018) acs.jced.8b00600, <https://doi.org/10.1021/acs.jced.8b00600>.
- [62] N. Nkosi, K. Tumba, S. Ramsuroop, Activity coefficients at infinite dilution of various organic solutes in the deep eutectic solvent (tetramethylammonium chloride + 1,6 hexanediol in the 1:1 molar ratio), *S. Afr. J. Chem. Eng.* 27 (2019) 7–15, <https://doi.org/10.1016/j.sajce.2018.11.003>.
- [63] L. Manyoni, G. Redhi, Separation potential of 1,5-pentanediol-based deep eutectic solvent: infinite dilution activity coefficients and excess thermodynamic data, *Heliyon* 9 (2023) e21516, <https://doi.org/10.1016/J.HELİYON.2023.E21516>.
- [64] L. Manyoni, G. Redhi, 1,6-hexanediol based deep eutectic solvent and their excess data at infinite dilution, *Chem. Thermodyn. Therm. Anal.* 8 (2022) 100088, <https://doi.org/10.1016/j.ctta.2022.100088>.