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A review on the thermal conductivity of deep eutectic solvents

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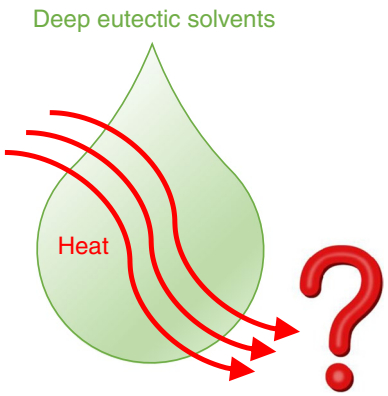
Abstract

Deep eutectic solvents may develop a pivotal role in future technologies considering sustainability and safety as pivotal aspects for chemistry developments. The possible application of these fluids for heat transfer operations is of great relevance for which the knowledge of thermal properties such as thermal conductivity is required as well as inferring structure–property relationships which allow reverse design of the fluids according to the technological requirements. Considering the technological relevance of this property, the available literature on the thermal conductivity for deep eutectic solvents is critically discussed showing strengths and weaknesses. The analysis of the state-of-the-art shows the future needs in this research field considering the application of these solvents for thermal-related technologies. The review indicates the scarcity of reliable experimental data and the need of predictive methods, which could be used for process design and solvent screening purposes. Likewise, considering the relevance of developing predictive methods for *in silico* design of these fluids according to industrial needs, the available predictive theoretical approaches are analysed showing their reliability as well as future needs. Finally, considering the need of developing suitable and reliable structure–property relationship, the molecular level basis of thermal conductivity in deep eutectic solvents is discussed, showing the role of hydrogen bonding and the effects rising from the involved hydrogen bond donors and acceptors as well as the eutectic compositions. This work reports the first literature review and analysis on thermal conductivity for deep eutectic solvents considering an experimental and theoretical approach as well as providing support for the molecular basis of this technologically relevant property, thus contributing to the development of environmentally friendly materials for thermal-related technologies.

Graphical abstract



Keywords Thermal conductivity · Deep eutectic solvents · Experimental data · Predictive modelling · Molecular features

Abbreviations

ChCl	Choline chloride
DES	Deep eutectic solvent
HBA	Hydrogen bond acceptor
HBD	Hydrogen bond donor
NADES	Natural deep eutectic solvent

List of symbols

a	Bridgman equation empirical parameter
λ	Thermal conductivity

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η	Viscosity
ρ	Density
T	Temperature
u	Speed of sound

Introduction

Deep eutectic solvents (DESs) [1] are formed by the eutectic mixture of two compounds, a hydrogen bond donor (HBA) and hydrogen bond acceptor (HBA). The HBA–HBD mixing at a suitable ratio lead to a system with melting point lower than those for the corresponding components [2]. Therefore, forming liquid systems at close to ambient temperature conditions [3], which can be used as solvents or heat transfer materials. The decrease in the melting point upon HBA/HBD mixing is produced by the development of strong hydrogen bonds [4]. Although there is some controversy in the literature for the definition of what a DESs is, we follow in this work the definition of DES based on Abbot's work [1], considering classical DES for which the HBA–HBD interaction through hydrogen bonding is a necessary condition.

The number of possible HBA/HBD combinations is extremely large, thus forming a new group of solvents (materials) with properties tuned by the suitable combination of HBA–HBD compounds to be applied in many technological challenges [5]. Likewise, there is a large group of natural HBA–HBD compounds, which may form DESs, leading to the so-called natural DES (NADES) [6], thus forming a suitable platform for developing environmentally friendly DESs [7].

The large attention attracted by DES is justified considering their promising physicochemical properties [8], which can be fine-tuned through suitable HBA–HBD combinations [9] to obtain environmentally friendly solvent profiles with low toxicity [10, 11] and biodegradability [12]. DES have been proposed to be used in different applications as solvents for solvent replacement studies [13]. Likewise, applications in pharmacology [14], as drug delivery vehicles [15], for gas capture operations [16] with the emphasis on CO_2 [17], bio-refining [18], fuels treatment [19], extraction operations [20], water treatment [21], or nanomaterials development [22]. Biodegradability and toxicity of DES–NADES [23, 24] is good enough to consider them as vehicles for pharmacological applications [25], and their effect on environment may be considered as minor [26]. Likewise, the possibility of developing DES from different HBA–HBD combinations, many of them with natural origin, is a competitive advantage for developing these fluids at low to moderate cost [27], in comparison with the closely related counterparts like ionic liquids [28]. Moreover, DES, and specially NADES, have proved suitable physicochemical properties [29], with densities, usually larger than water [30], moderate to large viscosity [31], which may hinder some of their possible applications but can be fine-tuned through composition effects or by mixing with organic solvents or water [32]. Likewise, DES have almost negligible vapour pressure [33], which consider them as suitable replacements of volatile organic compounds, a.k.a. VOCs [34]. Regarding the thermal properties [35], although the available information is still scarce and no systematic studies have been developed, the heat capacities of these fluids are large enough [36] for considering them as suitable fluids in many heat transfer applications [37]. The state-of-the art of DES physicochemical properties has been recently reviewed in different publications [38–41] showing their relevance for the application and scaling up of DESs for several types of technologies. These studies have probed that among the most relevant thermal properties of DES, thermal conductivity (λ) is crucial for their application in heat transfer operations [42], considering that these fluids have been proposed for several applications including their use as heat transfer fluids [43, 44]. Therefore, the development of systematic knowledge of thermal conductivity for DESs as a function of HBA–HBD types, temperature, and eutectic composition is pivotal for the advance in the possible industrial applications of DESs as alternative compounds to traditional heat transfer fluids. The available literature on thermal conductivity for DES is reviewed in this work with the objective of analysing understanding the state-of-the-art as well as the suitability of using these materials in thermal-related operations. The relationships between HBA–HBD composition and thermal conductivity is also analysed as well as the nanoscopic origin of this property with the objective of developing suitable micro- to macroscopic relationships for designing suitable DESs for thermal industrial operations. The novelty and need of this work may be summarized as follows:

(i) The critical review and analysis of thermal conductivity of DESs is reported for the first time in terms of physical conditions (temperature), composition (HBA–HBD components), and intermolecular forces.
(ii) The molecular level basis of this property is analysed for the first time.
(iii) The available predictive models are critically discussed in terms of their accuracy and performance.
(iv) A strengths and weaknesses analysis of the state-of-the-art for this property is reported for the first time with reported recommendations for future research directions and applications.
(v) The technological relevance of and accurate and systematic knowledge of thermal properties for DES require the reported analysis and discussion to show the current problems hindering scaling up as well as the possible solutions.

Experimental thermal conductivity database

Pure DESs

The available literature reporting experimental measurements for the thermal conductivity of DESs is summarized in Table 1. In spite of the relevance of thermal conductivity for the aforementioned applications, the reported data are still very scarce and mostly limited to choline chloride (ChCl)-containing DESs, with only 14 relevant publications in the 2016–2020 period. Most of the reported data were obtained using the transient hot wire method, thus leading to 3–5% accuracy for this type of fluids, as indicated in Table 1. The analysis of the literature shows the following needs: (i) extension of measurements to non-ChCl DESs, (ii) validation of transient hot wire method in comparison with other methods, and (iii) effect of purity on DESs thermal conductivity including absorbed water effect.

The analysis of the literature shows some of the most relevant DESs being reported in different literature sources showing different values, Fig. 1. The values for ChCl:urea or :glycerol or :ethylene glycol, all of them at 1:2 molar ratio, show differences across the literature but being in the 5% range, which may be considered reasonable in terms of fluids with different purities, i.e. water content, and experimental methodologies.

The data reported in Fig. 2 show the HBD effect on the thermal conductivity for ChCl-containing DES. The reported results indicate that although including different HBDs into the DES formulation lead to different thermal conductivity values, this effect is very minor considering that an average thermal conductivity of 0.208 W m^{-1} K^{-1} is inferred for all the considered ChCl-based DES, with just 0.017 W m^{-1} K^{-1} standard deviation, considering HBDs with very different molecular structures. Thus, HBA type determines the value of thermal conductivity with a minor effect considering the HBD type. Nevertheless, some exceptions were found in the literature, Gautam et al. [42] reported $\lambda = 0.245$ W m^{-1} K^{-1} for ChCl:urea (1:2) at 298.15 K whereas 0.182 W m^{-1} K^{-1} were reported for ChCl:thiourea (1:2) at the same temperature. Thus, the replacement of an oxygen atom for a sulphur one decreases the λ values, which may be justified considering the inverse relationship between λ and molar mass. Likewise, all the HBDs considered in Fig. 2 contain the same type of atoms (C,H,O) with the exception of thiourea, thus leading to lower λ for ChCl-based DESs.

Regarding the effect of HBA type, the scarcity of the literature does not allow to infer systematic conclusions. For closely related HBAs, the literature shows very minor effects. Gautam et al. [42] reported $\lambda = 0.245$ W m^{-1} K^{-1} for ChCl:urea (1:2) and $\lambda = 0.242$ W m^{-1} K^{-1} for diethylethanol ammonium:urea (1:2), both at 298 K. Likewise, Chen et al. [57] studied alkylammonium bromide:glycerol (1:2) reporting 0.217, 0.209, and 0.209 W m^{-1} K^{-1} at 293.15 K on going from ethyl to propyl to butyl, respectively, in the HBA. On the contrary, Chen et al. [57] studied ChCl:ethylene glycol and methyl-triphenylphosphonium bromide:ethylene glycol (1:3) reporting $\lambda = 0.195$ W m^{-1} K^{-1} and 0.168 W m^{-1} K^{-1} at 298.15 K, respectively, thus confirming that large changes in thermal conductivity are only obtained when involving structurally very different HBAs.

An additional factor to be considered for analysing DESs thermal conductivity is the HBA:HBD molar ratio. Although in a strictly thermodynamic sense, the eutectic composition is a single value for each HBA:HBD combination, different compositions around the true eutectic ones are considered for DESs development in the literature. Therefore, selected DES with different HBA:HBD molar ratios were considered and reported in Fig. 3. These results show almost negligible effect of HBA:HBD *i*:*j* molar ratios on thermal conductivity, with increasing HBD content in the DESs leading to almost the same thermal conductivity data for a fixed HBA.

The temperature effect on DESs thermal conductivity was also analysed. Results in Fig. 4 show temperature evolution of thermal conductivity for ChCl-based DESs. According to the theory of molecular liquids [50], the thermal conductivity should decrease when intermolecular distance increases, i.e. with increasing temperature. Nevertheless, results in Fig. 4 show more complex behaviour. The available literature shows severe discrepancies between the available sources even for the most common DESs included in Fig. 4. In the case of ChCl:urea (1:2), decreasing thermal conductivity with increasing temperature is inferred, following a linear behaviour. Nevertheless, the ($d\lambda/dT$) slope is very different considering the literature sources, Fig. 4a. Values from Ibrahim et al. [50] show negligible variations, below the measurement uncertainties, with temperature whereas Gautam et al. [42] reported a large decrease with increasing temperature. The cause of these large discrepancies may be on the purity of the samples, including water content, and on the experimental methods. Negative slope is also inferred for ChCl:ethylene glycol (1:2), Fig. 4c. Likewise, positive ($d\lambda/dT$) slopes are inferred for some DESs as for ChCl:glycerol (1:2) reported in Fig. 4b but with large discrepancies considering the different literature sources. Positive ($d\lambda/dT$) slopes have been reported in the literature for other types of DESs such as ChCl:lactic acid [51], or methyl-triphenylphosphonium bromide:ethylene glycol [60]. For non-ChCl-based DES, studies on temperature effect are very scarce, and in some cases like alkylammonium bromide:glycerol [56], thermal conductivity remains constant for the studied temperature ranges (30 °C). Therefore, the temperature effect

Table 1 The literature sources reporting experimental measurements of thermal conductivity for DES. For each DES, the involved HBA:HBD components are reported as well as the corresponding molar ratio (*i*:*j*)

Reference*	Year	DES	*T*/K	Method	Uncertainty
Lan et al. [45]	2022	Choline chloride:ethylene glycol (1:5) (1:6) (1:7) (1:8)	298–328	Transient hot wire	±4%
Jafari et al. [46]	2022	Choline chloride:ethylene glycol (1:2) (1:5)	283–333	Transient hot wire	±5%
Chen et al. [47]	2021	Betaine:glycerol (1:2) (1:3) (1:4) (1:5) (1:6) Betaine:1,2-propanediol (1:3.5) (1:4) (1:6) (1:6)	293–372	Transient hot wire	n.r. [a]
Albayati et al. [48]	2021	Choline chloride:glycerol (1:2) Choline chloride:ethylene glycol (1:2) Ammonium acetate:lactic acid (1:1) (1:2) (1:3) Ammonium acetate:glycerol (1:2) Potassium carbonate:glycerol (1:6) (1:8) (1:10)	298–333	Transient hot wire	±5%
Yu et al. [49]	2021	Menthol:decanoic acid (4:1) (2.3:1) (1.5:1) (1:1) (1:1.5) (1:2.3)	293–363	Transient hot wire	±2%
Ibrahim et al. [50]	2020	Choline chloride:urea (1:2) Choline chloride:glycerol (1:2) Choline chloride:ethylene glycol (1:2) Choline chloride:triethylene glycol (1:3) Choline chloride:malonic acid (1:1) Choline chloride:d-fructose (2:1) Choline chloride:d-glucose (2:1)	298–363	Transient plane	±0.001 W m^{-1} K^{-1}
Gautam et al. [42]	2020	Choline chloride:urea (1:2) N,N-diethyl ethanol ammonium chloride + urea (1:2) choline chloride:thiourea (1:2)	298–343	Transient hot wire	±3%
Liu et al. [37]	2019	Choline chloride:glycerol (1:2) (1:3) (1:4) (1:5)	305–335	Transient hot wire	±3%
Alcalde et al. [51]	2019	Choline chloride:lactic acid (1:1) (1:1.5) (1:2) (1:2.5)	298	transient hot wire	±5%
Rogosic et al. [52]	2019	Choline chloride:ethylene glycol (1:2) (1:3) (1:3.5)	298	Transient hot bridge	n.r.[a]
Dehury et al. [43]	2018	DL-menthol:oleic acid (1:1)	298–373	Transient hot wire	n.r.[a]
Singh et al. [53]	2018	Choline chloride:glycerol (1:2) (1:3) (1:4) (1:5) Choline chloride:glycerol:PEG600 (1:3:2) (1:4:2) (1:5:2)	298–373	Transient hot wire	±5%
Alcalde et al. [54]	2018	Choline chloride:lactic acid (1:1)	303	Transient hot wire	±5%
Kucan et al. [55]	2018	Choline chloride:glycerol (1:1.5) (1:2) (1:3)	298	Transient hot bridge	n.r.[a]
Chen et al. [56]	2017	Ethyl ammonium bromide:glycerol (1:2) Propyl ammonium bromide:glycerol (1:2) Butyl ammonium bromide:glycerol (1:2)	293–323	Transient hot wire	n.r.[a]
Chen et al. [57]	2017	Choline chloride:ethylene glycol (1:3) (1:4) (1:5) Choline chloride:triethylene glycol (1:3) (1:4) (1:5) Methyl-triphenylphosphonium bromide:ethylene glycol (1:3) (1:4) (1:5) Methyl-triphenylphosphonium bromide:triethylene glycol (1:4) (1:5)	298–323	Transient hot wire	±5%
Yan et al. [58]	2017	Choline chloride:ethylene glycol (1:3) (1:4) (1:5) Choline chloride:triethylene glycol (1:3) (1:4) (1:5) Methyl-triphenylphosphonium bromide:ethylene glycol (1:3) (1:4) (1:5) Methyl-triphenylphosphonium bromide:triethylene glycol (1:3) (1:4) (1:5)	298–323	Transient hot wire	n.r.[a]
Sander et al. [59]	2016	Choline chloride:urea (1:2) Choline chloride:glycerol (1:2)	298	Transient hot bridge	n.r.[a]
Fang et al. [60]	2016	Choline chloride:ethylene glycol (1:1.75) (1:2) Choline chloride:triethylene glycol (1:2.5) (1:3) (1:4) (1:5) Methyl-triphenylphosphonium bromide:ethylene glycol (1:3) (1:4) (1:5)	298–343	Transient hot wire	±5%

[a]Not reported

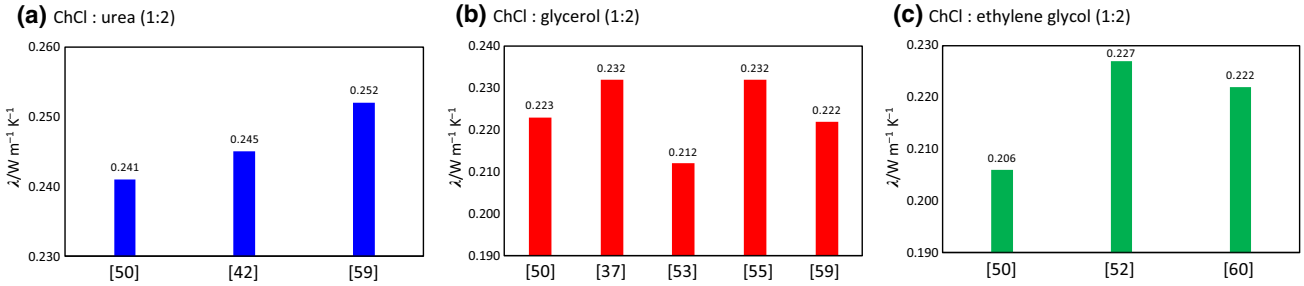

Fig. 1 Experimental thermal conductivity, λ, at 298 K for the reported DESs from different literature sources

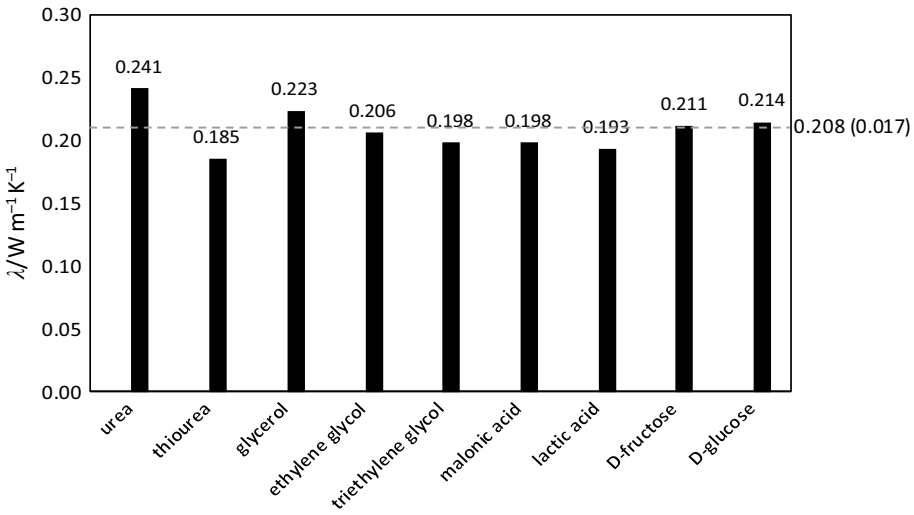

Fig. 2 Experimental thermal conductivity, λ, for ChCl:HBD at 298.15 K from Ibrahim et al. [50]. Grey dashed line indicates average value (standard deviation) for the reported DESs

on thermal conductivity for DESs is still not well understood, and there is a certain need of additional studies for (i) inferring the sign of ($d\lambda/dT$) slopes in terms of the involved HBA:HBD compounds and (ii) determining the values of ($d\lambda/dT$) slopes, which, in most of the reported literature studies, are below the experimental uncertainty.

Modelling and prediction of thermal conductivity

The development of theoretical models for predicting the thermal conductivity of DESs is required considering the large number of possible HBA:HBD combinations as well as for screening purposes to find the most suitable molecular combinations for DESs thermal applications. The Bridgman equation [61] is a semiempirical model which allows to calculate thermal conductivity, from molar volume (i.e. density) and speed of sound, Eq. [1]:

$$\lambda = a\left(\frac{N_A}{V}\right)^{2/3} k_B u \quad (1)$$

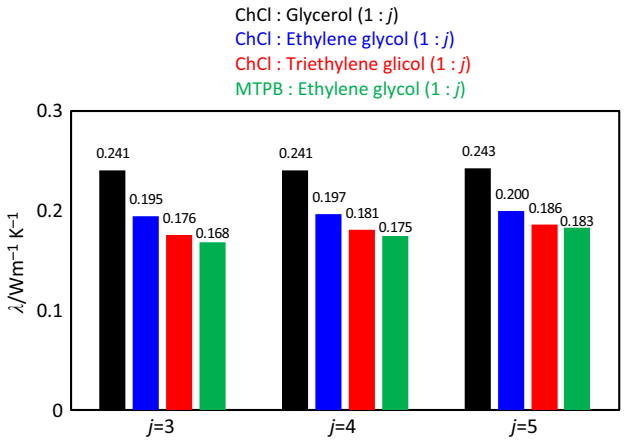

Fig. 3 Experimental thermal conductivity, λ, for ChCl:HBD (1:j) at 305 K (for ChCl:glycerol [44]) or 298.15 K (remaining DESs [57]) as a function of j. MTPB stands for methyl-triphenylphosphonium bromide

where a stands for an empirical parameter, N_A stands for the Avogadro number, V stands for the molar volume, k_B stands for the Boltzmann's constant, and u stands for the

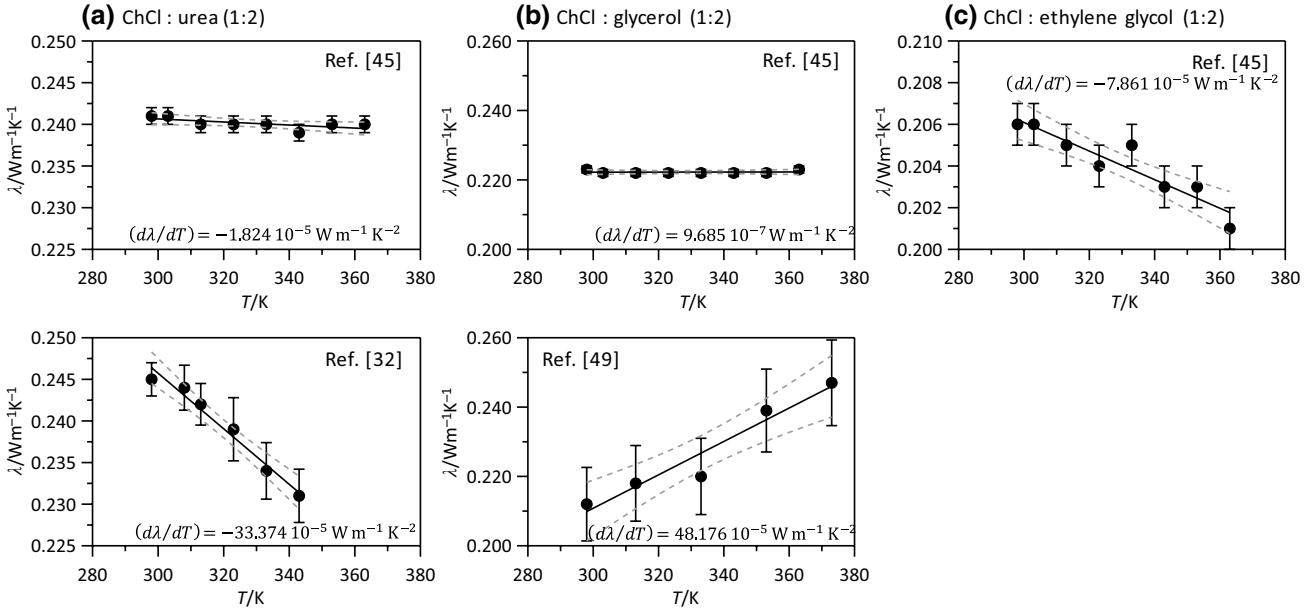

Fig. 4 Temperature, T, effect on thermal conductivity, λ, for selected DESs. Continuous lines show linear fits, with the slope indicated inside each plot. Dashed lines show 99% confidence interval of the linear fits

speed of sound. Thus, this model allows to predict λ, which is a property difficult to be measured and usually reported with large uncertainties, with two easily available properties such as density and speed of sound. Nevertheless, the available literature information on density and speed of sound also shows non-negligible discrepancies. Results in Fig. 5a show experimental density data for ChCl:urea (1:2) with some literature sources showing relevant differences with other ones. Likewise, the literature on DESs speed of sound is also scarce and large differences between the available sources are inferred, Fig. 5b. Therefore, uncertainties in the use of Bridgman equation may rise from the differences in the available density and speed of sound data.

A relevant issue in the application of Eq. (1) for predictive purposes stands on the value of a factor, which is frequently considered as $a = 3.0$. The results of the application of Bridgman model for some selected ChCl-based DESs are reported in Fig. 6. Two different a values were considered ($a = 3$ or 4), with the model leading to poor predictions for $a = 3$ and excellent results for $a = 4$. Therefore, the model works properly for the selection of a suitable a factor.

Despite the relevance of developing predictive models for thermal conductivity, the available modelling studies are very scarce in the literature. Considering that thermal conductivity is a dynamic property, the possible relationship with viscosity may be considered, as previously done for ionic liquids [68], according to Eq. (2) based on the Mohanty theory [69]:

$$\frac{M\lambda}{\eta} = \text{constant} \tag{2}$$

where M stands for the molar mass, and η stands for the dynamic viscosity. The development of λ versus η relationships has a relevant problem on the available η data from the literature. Results in Fig. 5c show literature η data for ChCl:urea (1:2) DES at 298.15 K from different sources showing large differences. Although the main reason behind the fluctuation on η data is not certain, it is most likely due to different DES purities, experimental methodologies or unknown factors not properly reported in the corresponding literature sources (e.g. poor calibration). This situation has been previously reported for many different types of DESs [8] and currently hinders a systematic evaluation of λ versus η relationships. Nevertheless, the possibility of DESs fulfilling Eq. (2) was analysed for several selected ChCl-based DESs, Fig. 7a. These results discard a suitable fulfilling of Eq. (2) even for the most studied DESs, with the linear relationship mostly discarded. Likewise, the application of Eq. (2) for ionic liquids [68] showed a quasilinear evolution with negative slope, whereas results in Fig. 7a show positive slope for ChCl-based DESs. The analysis of the direct relationship between dynamic viscosity and thermal conductivity is reported in Fig. 7b, showing a nonlinear evolution but inferring that increasing viscosity leads to an increase in thermal conductivity. This behaviour can be attributed to an increase in intermolecular forces (hydrogen bonding) as the origin of increasing viscosity, which maintain the

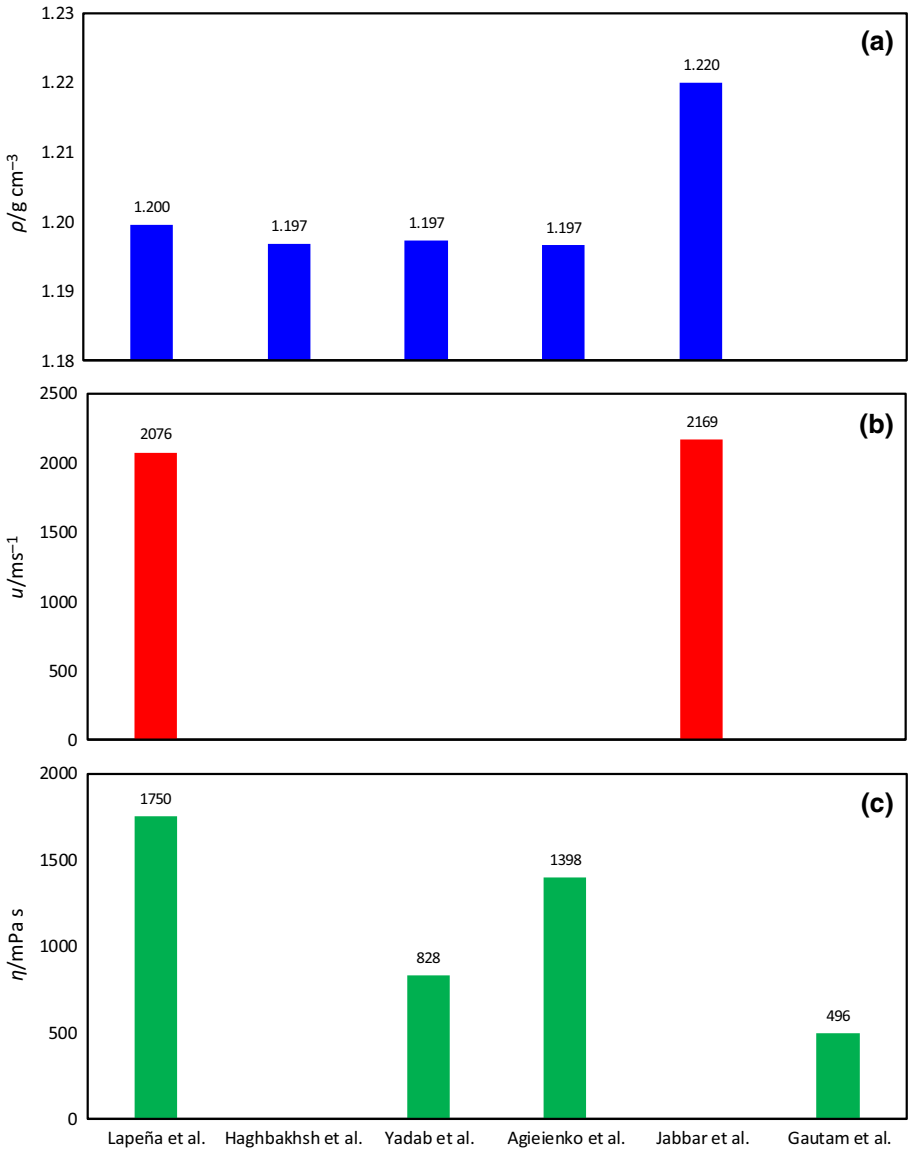

Fig. 5 Experimental density, ρ, speed of sound, u, and dynamic viscosity, η, for ChCl:urea (1:2) at 298.15 K from different literature sources. Lapeña et al. [62], Haghbakhsh et al. [63], Yadab et al. [64], Agieienko et al. [65], Jabbar et al. [66], and Gautam et al. [67]

molecules closely packed together, thus leading to a larger thermal conductivity. Nevertheless, considering the complexity of intermolecular forces in DESs, in terms of type and extension [70], a complex η versus λ relationship may be expected as reported in Fig. 7b. The development of these η versus λ models would require the availability of accurate and reliable viscosity data, which, at the current state, are not available in the literature, Fig. 5c.

Regarding the modelling of the temperature evolution of thermal conductivity and its possible relationship with viscosity evolution, the available results show large decrease in viscosity upon increasing temperature whereas thermal conductivity suffers minor changes upon heating, Fig. 4, i.e. $(d\lambda/dT) << (d\eta/dT)$. Thus, the η versus λ representation in Fig. 8 for ChCl:urea (1:2) does not show any relationship, and although both are dynamic properties, the decrease in viscosity upon heating, as a consequence of the weakening of intermolecular forces and increase in the average intermolecular distance is not accompanied by a large decrease in thermal conductivity, Figs. 4 and 8. It should be remarked that some authors have reported thermal conductivity increasing with temperature, Fig. 4b, whereas DESs viscosity always decreases with increasing temperature [73].

Additional attempts to develop predictive models for DESs thermal conductivity are almost absent in the literature. Ibrahim et al. [50] reported a model, so-called extended Wu model [EWM], which was used for the estimation of ChCl-based DESs thermal conductivity. This model used the Wu approach [74], and it is based on a group contribution approach, which requires parameters for (i) the determination of boiling and critical temperatures of DESs and (ii) for the determination of λ_0 parameters of the model.

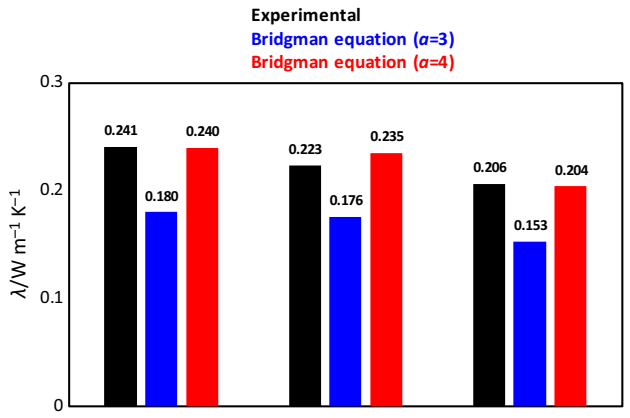

Fig. 6 Thermal conductivity, λ, for ChCl:HBD (1:2) at 298 K from experimental data (Ibrahim et al. [50]) and those calculated from Bridgman equation, with two different a values (Eq. 1), from experimental density and speed of sound obtained in the literature (Ref. [66])

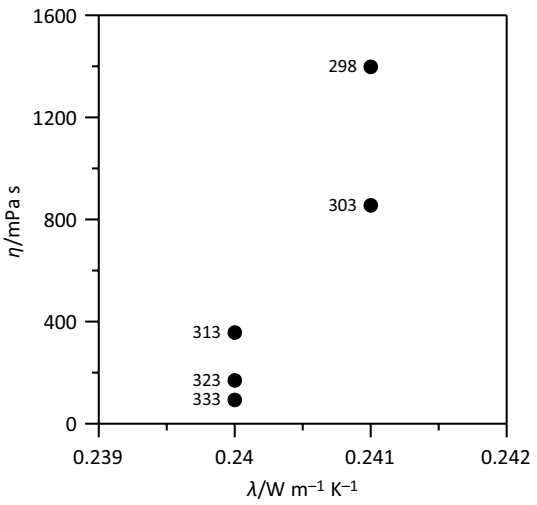

Fig. 8 Relationship between thermal conductivity, λ, and dynamic viscosity, η, for ChCl:urea (1:2) as a function of temperature indicated inside the plot. Experimental values from [50, 65]

Likewise, this model considers a DESs as a mixture of two components, and thus, the thermal conductivity of the mixture (DESs) is obtained from those of the components (HBAs and HBDs) using suitable mixing rules and correlative parameters, which need to be adjusted to experimental data. Therefore, although the model led to deviations with experimental data lower than 2%, it requires a large number of group contribution parameters, which are available only for selected compounds, as well as experimental data for the mixing rules, i.e. it is not a purely predictive model, and thus, it may have limited practical application. A recent review on the modelling of thermodynamic and transport properties of DESs did not include any relevant effort for thermal conductivity prediction [75]. From the molecular level viewpoint, molecular simulation studies may provide information on the nanoscopic roots of thermal conductivity in DESs. Nevertheless, these modelling studies are very scarce in the literature. In a recent work, Celebi et al. [76] reported a molecular dynamics (MD) study on thermal conductivity for aqueous solutions of DES. These authors probed the role of the nature and strength of HBA–HBD hydrogen bonding on the values of thermal conductivity. Likewise, the negligible effect of temperature was confirmed as well as the large effect of water content as it affects the extension of DESs hydrogen bonding. Although molecular modelling studies on the relationships between thermal conductivity and intermolecular forces (hydrogen bonding) are scarce in the literature, the previous studies have showed the relevance of hydrogen bonding for dynamic properties such as viscosity or self-diffusion coefficients. The studies by Perkins et al. [77, 78] and Celebi et al. [79] probed that the

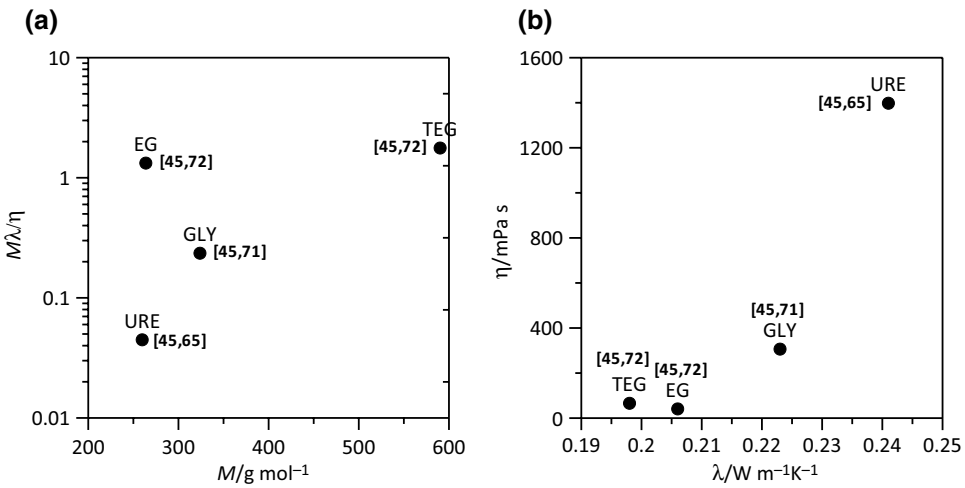

Fig. 7 **a** Results for ChCl-based DESs for testing the Mohanty model and **b** viscosity versus thermal conductivity for the same DESs. All values at 298.15 K. Thermal conductivity data from Ref. [50] and viscosity data from the reported sources (Refs. [65 [71, 72]]). The considered DESs are ChCl:urea (URE) (1:2), ChCl:glycerol (GLY) (1:2), ChCl:ethylene glycol (EG) (1:2), and ChCl:triethylene glycol (TEG) (1:3)

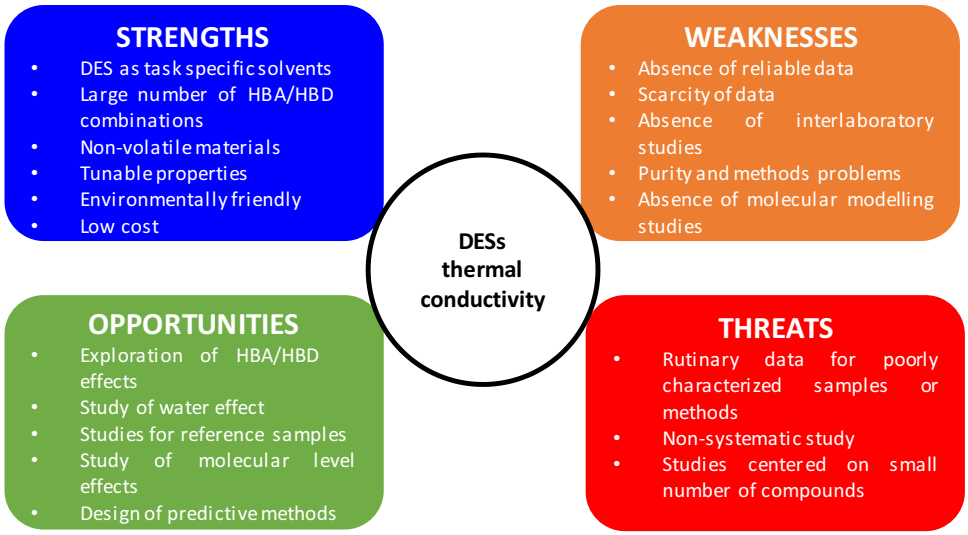

Fig. 9 SWOT analysis of thermal conductivity for DESs

nature, extension, and strength of the HBA–HBD hydrogen bonding determine the values of dynamic properties, with a common trend to maximize the hydrogen bonding network between the different molecular moieties. Therefore, there is a crucial need for developing accurate predictive approaches, based on the reliable understanding of molecular level effects controlling the property, considering the large number of HBA:HBD combinations leading to DESs as well as the validity of DESs for thermal engineering applications.

Conclusions

The analysis of the available literature on thermal conductivity for deep eutectic solvents had led to several conclusions:

(i) The available data are mostly limited to choline chloride-based solvents with scarce studies on other types of systems.
(ii) The temperature effect on thermal conductivity should be clarified, considering that minor changes are inferred for most of the systems and increasing or decreasing values are obtained upon heating.
(iii) The main effect on the property is caused by the type on considered hydrogen bond acceptor. In order to infer on the role of the hydrogen bond donor, more data are required.
(iv) The relationship with other relevant properties, especially viscosity, is not clarified considering the large differences among the values reported from different sources.
(v) Predictive models have not been reported in the literature, thus limiting the applicability of the considered solvents.

Therefore, the following recommendations have been made for developing a detailed analysis on the thermal properties of DESs:

(i) Systematic studies on selected groups of deep eutectic solvents, considering different groups of hydrogen bond donors and acceptors are required.
(ii) The purity and water content of the DES samples should be fully clarified, and their effect on thermal conductivity should be reported.
(iii) The studies should be carried out in wider temperature ranges using highly accurate experimental methods with reduced experimental uncertainties.
(iv) Predictive models should be developed, for which group contribution approaches following a parallel effort to ionic liquids could be considered as a suitable starting point.
(v) Molecular modelling studies, mainly molecular dynamics, should be developed for analysing the relationship between molecular structures of hydrogen bond donors–acceptors, nature and extension of hydrogen bonding, and thermal conductivity, thus allowing to infer the molecular level and nanoscopic roots of this property.

A strengths, weaknesses, opportunities, and threats (SWOT) analysis is included in Fig. 9 to summarize the conclusions obtained in this work.

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Declarations

Conflicts of interest The authors whose names are listed immediately below certify that they have no affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licencing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge, or beliefs) in the subject matter or materials discussed in this manuscript.

References

1. Smith EL, Abbott AP, Ryder KS. Deep eutectic solvents (DESs) and their applications. Chem Rev. 2014;114:11060–82.
2. Alhadid A, Mokrushina L, Minceva M. Design of deep eutectic systems: a simple approach for preselecting eutectic mixture constituents. Molecules. 2020;25:1077.
3. Kollau LJBM, Vis M, van der Bruinhorst A, Esteves ACC, Tuinier R. Quantification of the liquid window of deep eutectic solvents. Chem Comm. 2018;54:13351–4.
4. Wang H, Liu S, Zhao Y, Wang J, Yu Z. Insights into the hydrogen bond interactions in deep eutectic solvents composed of choline chloride and polyols. ACS Sustain Chem Eng. 2019;7:7760–7.
5. Florindo C, Lima F, Dias-Ribeiro B, Marrucho IM. Deep eutectic solvents: overcoming 21st century challenges. Curr Opin Green Sustain Chem. 2019;18:31–6.
6. Paiva A, Craveiro R, Aroso I, Martins M, Reis RL, Duarte ARC. Natural deep eutectic solvents–solvents for the 21st century. ACS Sus Chem Eng. 2014;2:1063–71.
7. Liu Y, Friesen B, McAlpine JB, Lankin DC, Chen SN, Pauli GF. Natural deep eutectic solvents: properties, applications, and perspectives. J Nat Prod. 2018;81:679–90.
8. García G, Aparicio S, Ullah R, Atilhan M. Deep eutectic solvents: physicochemical properties and gas separation applications. Energy Fuels. 2015;29:2616–44.
9. Wojeicchowski JP, Ferreira AM, Abranches SO, Mafra MR, Coutinho JAP. Using COSMO-RS in the design of deep eutectic solvents for the extraction of antioxidants from rosemary. ACS Sustain Chem Eng. 2020;8:12132–41.
10. Kumar A, Codeiro MNDS. Probing the environmental toxicity of deep eutectic solvents and their components: an in silico modeling approach. ACS Sustain Chem Eng. 2019;7:10649–60.
11. Macario IPE, Oliveira H, Menezes AC, Ventura SPM, Pereira JL, Goncalves AMM, Coutinho JAP, Goncalves FJM. Cytotoxicity profiling of deep eutectic solvents to human skin cells. Sci Rep. 2019;9:3932.
12. Juneidi I, Hayyan M, Hashim MA. Evaluation of toxicity and biodegradability for cholinium-based deep eutectic solvents. RSC Adv. 2015;5:83636–47.
13. Perna FP, Vitale P, Capriati V. Deep eutectic solvents and their applications as green solvents. Curr Opin Green Sustain Chem. 2020;21:27–33.
14. Emani S, Shayanfar A. Deep eutectic solvents for pharmaceutical formulation and drug delivery applications. Pharma Dev Technol. 2020;25:779–96.
15. Zainal-Abidin MH, Hayyan M, Nhoh GC, Wong WF, Looi CY. Emerging frontiers of deep eutectic solvents in drug discovery and drug delivery systems. J Control Release. 2019;316:168–95.
16. Chen Y, Han X, Liu Z, Yu D, Guo W, Miu T. Capture of toxic gases by deep eutectic solvents. ACS Sustain Chem Eng. 2020;8:5410–30.
17. Liu Y, Yu H, Sun Y, Zeng S, Zhang X, Nie Y, Zhang S, Ji X. Screening deep eutectic solvents for CO_2 capture with COSMO-RS. Front Chem. 2020;8:82.
18. Bradic B, Novak U, Lizokar B. Crustacean shell bio-refining to chitin by natural deep eutectic solvents. Green Process Synth. 2020;9:13–25.
19. Jha D, Haider MB, Kumar R, Balathanigaimani MS. Extractive desulfurization of fuels using diglycol based deep eutectic solvents. J Environ Chem Eng. 2020;8: 104182.
20. Soltanmohammadi F, Jouyban A, Shayanfar A. New aspects of deep eutectic solvents: extraction, pharmaceutical applications, as catalyst and gas capture. Chem Pap. 2020;75:439–53.
21. Florindo C, Monteiro NV, Ribeiro BD, Branco LC, Marrucho IM. Hydrophobic deep eutectic solvents for purification of water contaminated with Bisphenol-A. J Mol Liq. 2020;297: 111841.
22. Abo-Hamad A, Hayyan M, Al-Saadi MA, Hashim MA. Potential applications of deep eutectic solvents in nanotechnology. Chem Eng J. 2015;273:551–67.
23. Halder AK, Cordeiro MNDS. Probing the environmental toxicity of deep eutectic solvents and their components: an in silico modeling approach. ACS Sustain Chem Eng. 2019;7:16049–10660.
24. Yang Z. Toxicity and Biodegradability of deep eutectic solvents and natural deep eutectic solvents. In: Ramon DJ, Guillena G, editors. Deep eutectic solvents: synthesis, properties and applications. Weinheim: Wiley-VDH; 2020.
25. Palmelund H, Andersson MP, Asgreen CJ, Boyd BJ, Rantanen J, Löbmann K. Tailor-made solvents for pharmaceutical use? Experimental and computational approach for determining solubility in deep eutectic solvents (DES). Int J Pharma X. 2019;1: 100034.
26. Torregros-Crespo J, Marset X, Guillena G, Ramón DJ, Martínez-Espinosa RM. New guidelines for testing "Deep eutectic solvents" toxicity and their effects on the environment and living beings. Sci Total Environ. 2020;704: 135382.
27. Cruz H, Jordao N, Brnaco LC. Deep eutectic solvents (DESs) as low-cost and green electrolytes for electrochromic devices. Green Chem. 2017;19:1653–8.
28. Plotka-Wasylka J, de la Guardia M, Andruch V, Vilkova M. Deep eutectic solvents vs ionic liquids: similarities and differences. Microchem J. 2020;159: 105539.
29. Gajardo-Parra NF, Lubben MJ, Winnert JM, Leiva A, Brennecke JF, Canales RI. Physicochemical properties of choline chloride-based deep eutectic solvents and excess properties of their pseudo-binary mixtures with 1-butanol. J Chem Thermodyn. 2019;133:272–84.

30. Haghbakhsh R, Bardool R, Bakhtyari A, Duarte ARC, Raeissi S. Simple and global correlation for the densities of deep eutectic solvents. J Mol Liq. 2019;296: 111830.
31. Bakhtyari A, Haghbakhsh R, Duarte ARC, Raeissi S. A simple model for the viscosities of deep eutectic solvents. Fluid Phase Equilibr. 2020;521: 112662.
32. Liu X, Fu N, Zhang Q, Cia S, Wang Q, Han D, Tang B. Green tailoring with water of choline chloride deep eutectic solvents for the extraction of polyphenols from palm samples. J Chromatogr Sci. 2019;57:272–8.
33. Shahbaz K, Mjalli FS, Vakili-Nezhaad G, AlNashef I, Asadov A, Farid MM. Thermogravimetric measurement of deep eutectic solvents vapor pressure. J Mol Liq. 2016;222:61–6.
34. Liu P, Hao JW, Mo LP, Zhang ZH. Recent advances in the application of deep eutectic solvents as sustainable media as well as catalysts in organic reactions. RSC Adv. 2015;5:48675–704.
35. Craveiro R, Aroso I, Flammia V, Carvalho T, Viciosa MT, Dionisio MT, Barreiros S, Reis RL, Duarte ARC, Paiva A. Properties and thermal behavior of natural deep eutectic solvents. J Mol Liq. 2016;215:534–40.
36. Taherzadeh M, Haghbakhsh R, Duarte ARC, Raeissi S. Estimation of the heat capacities of deep eutectic solvents. J Mol Liq. 2020;307: 112940.
37. Liu C, Fang H, Zhao J, Rao Z. Properties and heat transfer mechanistic study of glycerol/choline chloride deep eutectic solvents based nanofluids. Int J Heat Mass Trans. 2019;138:690–8.
38. Hansen BB, Spittle S, Chen B, Poe D, Zhang Y, Klein JM, Horton A, Adhikari L, Zelovich T, Doherty BW, Gurkan B, Maginn EJ, Ragauskas A, Dadmun M, Zawoddzinski TA, Baker GA, Tuckerman ME, Savinelli RF, Sangoro JR. Deep eutectic solvents: a review of fundamentals and applications. Chem Rev. 2021;121:1232–85.
39. Jafari K, Fatemi MH, Estellé P. Deep eutectic solvents (DESs): a short overview of the thermophysical properties and current use as base fluid for heat transfer nanofluids. J Mol Liq. 2021;321: 114752.
40. Omar KA. Sadeghi, physicochemical properties of deep eutectic solvents: a review. J Mol Liq. 2022;360: 119524.
41. Ijardar SP, Singh V, Gardas RL. Revisiting the physicochemical properties and applications of deep eutectic solvents. Molecules. 2022;27:1368.
42. Gautam RK, Seth D. Thermal conductivity of deep eutectic solvents. J Thermal Anal Calorim. 2020;140:2633–40.
43. Dehury P, Singh J, Banerjee T. Thermophysical and forced convection studies on (alumina + menthol)-based deep eutectic solvents for their use as a heat transfer fluid. ACS Omega. 2018;3:18016–27.
44. Liu C, Fang H, Qiao Y, Zhao J, Rao Z. Properties and heat transfer mechanistic study of glycerol/choline chloride deep eutectic solvents based nanofluids. Int J Heat Mass Trans. 2019;138:690–8.
45. Lan T, Xu J, Wang C, Li X, He M. The effect of water on the thermal conductivities of deep eutectic solvents (choline chloride + ethylene glycol) using two-wire structure 3ω method. J Mol Liq. 2022;359: 119330.
46. Jafari K, Fatemi MH, Lugo L. An experimental study of novel nanofluids based on deep eutectic solvents (DESs) by Choline chloride and ethylene glicol. J Mol Liq. 2022;360: 119521.
47. Chen Q, He N, Fan J, Song F. Thermal conductivity of betaine-glycerol, betaine-1,2-propanediol based deep eutectic solvents. Thermochim Acta. 2021;706: 179055.
48. Albayati N, Kadhom M, Abdullah G, Salih S. thermal conductivity of room temperature deep eutectic solvents. J Thermal Sci. 2021;30:1960–72.
49. Yu LY, Hou XJ, Wu KJ, He CH. Measurements of the thermal conductivity of L-menthol-decanoic acid deep eutectic solvents in the temperature range from 283.15 to 363.15 K at pressures up to 15 MPa. J Chem Eng Data. 2021;66:2061–70.
50. Ibrahim TH, Sabri MA, Jabbar NA, Nancarrow P. Thermal conductivity of choline chloride-based deep eutectic solvents and their mixtures with water: measurement and estimation. Molecules. 2020;25:3816.
51. Alcalde R, Gutiérrez A, Atilhan M, Aparicio S. An experimental and theoretical investigation of the physicochemical properties on choline chloride–lactic acid based natural deep eutectic solvent (NADES). J Mol Liq. 2019;290: 110916.
52. Rogosic M, Kucan KC. Deep eutectic solvents based on choline chloride and ethylene glicol as media for extractive desnitrification/dearomatization of motor fuels. J Ind Eng Chem. 2019;72:87–99.
53. Singh A, Walvekar R, Khalid M, Wong WY, Gupta TCSM. Thermophysical properties of glycerol and polyethylene glycol (PEG600) based DES. J Mol Liq. 2018;252:439–44.
54. Alcalde R, Atilhan M, Aparicio S. On the properties of (choline chloride + lactic acid) deep eutectic solvent with methanol mixtures. J Mol Liq. 2018;272:815–20.
55. Kucan K, Rogosic M. Purification of motor fuels by means of extraction using deep eutectic solvents based on choline chloride and glycerol. J Chem Technol Biotechnol. 2019;94:1282–93.
56. Chen Z, Ludwig M, Warr GG, Atkin R. Effect of cation alkyl chain on surface and physical properties in deep eutectic solvents. J Colloid Inter Sci. 2017;494:373–9.
57. Chen YY, Walvekar R, Khalid M, Shahbaz K, Gupta TCSM. Stability and thermophysical studies on deep eutectic solvent based carbon nanotube nanofluid. Mater Res Express. 2017;4: 075028.
58. Yan YC, Rashmi W, Khalid M, Shahbaz K, Gupta TCSM, Mase N. Potential application of deep eutectic solvents in heat transfer application. J Eng Sci Technol. 2017;5:1–14.
59. Sander A, Rogosic M, Slivar A, Zuteg B. Separation of hydrocarbons by means of liquid-liquid extraction with deep eutectic solvents. Solvent Extr Ion Exc. 2016;34:86–98.
60. Fang YK, Osama M, Rashmi W, Shahbaz K, Khalid M, Mjalli FS, Farid MM. Synthesis and thermo-physical properties of deep eutectic solvent-based graphene nanofluids. Nanotechnology. 2016;27: 075702.
61. Yebra F, Troncosos J, Romanín L. Thermal conductivity of ionic liquids under pressure. Fluid Phase Equilibr. 2020;515: 112573.
62. Lapeña D, Bergua F, Lomba L, Giner B, Lafuente C. A comprehensive study of the thermophysical properties of reline and hydrated reline. J Mol Liq. 2020;303: 112679.
63. Haghbakhsh R, Raeissi S. Densities and volumetric properties of (choline chloride + urea) deep eutectic solvent and methanol mixtures in the temperature range of 293.15–323.15 K. J Chem Thermodyn. 2018;124:10–20.
64. Yadav A, Pandey S. Densities and viscosities of (choline chloride + Urea) deep eutectic solvent and its aqueous mixtures in the temperature range 293.15 K to 363.15 K. J Chem Eng Data. 2014;59:2221–9.
65. Agieienko V, Buchner R. Densities, viscosities, and electrical conductivities of pure anhydrous reline and its mixtures with water in the temperature range (293.15 to 338.15) K. J Chem Eng Data. 2019;64:74.
66. Jabbar NMA, Mjalli FS. Ultrasonic study of binary aqueous mixtures of three common eutectic solvents. Phys Chem Liq. 2019;57:1–18.
67. Gautam RK, Ahmed SA, Seth D. Photophysics of thioflavin T in deep eutectic solvents. J Lum. 2018;198:508–16.
68. Tomida D, Kenmochi S, Tsukada T, Qiao K, Yokoyama C. Thermal conductivities of bmimPF_6, hmimPF_6, and omimPF_6 from 294 to 335 K at pressures up to 20 MPs. Int J Thermophys. 2007;28:1147–60.

69. Mohanty SR. A relationship between heat conductivity and viscosity of liquids. Nature. 1951;168:42.
70. Kaur S, Malik A, Kashyap HK. Anatomy of microscopic structure of ethaline deep eutectic solvent decoded through molecular dynamics simulations. J Phys Chem B. 2019;123:8291–9.
71. AlOmar MK, Hayyan M, Alsaadi MA, Akib S, Hayyan A, Hashim MA. Glycerol-based deep eutectic solvents: physical properties. J Mol Liq. 2016;215:98–103.
72. Mjalli FS, Naser J. A viscosity model for choline chloride-based deep eutectic solvents. Asia Pac J Chem Eng. 2015;10:273–81.
73. Haghbakhsh R, Parvaneh K, Raeissi S, Shariati A. A general viscosity model for deep eutectic solvents: the free volume theory coupled with association equations of state. Fluid Phase Equilibr. 2018;470:193–202.
74. Wu KJ, Zhao CX, He CH. Development of a group contribution method for determination of thermal conductivity of ionic liquids. Fluid Phase Equilibr. 2013;339:10–4.
75. Gonzalez de Castilla A, Bittner JP, Müller S, Jakobtorweihen S, Smirnova I. Thermodynamic and transport properties modeling of deep eutectic solvents: a review on g^E-models, equations of state, and molecular dynamics. J Chem Eng Data. 2020;65:943–67.
76. Celebi AT, Vlugt TJH, Moultos OA. Thermal conductivity of aqueous solutions of reline, ethaline, and glyceline deep eutectic solvents; a molecular dynamics simulation study. Mol Phys. 2021;119: e1876263.
77. Perkins AL, Painter P, Colina CM. Molecular dynamic simulations and vibrational analysis of an ionic liquid analogue. J Phys Chem B. 2013;117:10250–60.
78. Perkins SL, Painter P, Colina CM. Experimental and computational studies of choline chloride-based deep eutectic solvents. J Chem Eng Data. 2014;59:3652–62.
79. Celebi AT, Vlugt TJH, Moultos OA. Structural, thermodynamic, and transport properties of aqueous reline and ethaline solutions from molecular dynamics simulations. J Phys Chem B. 2019;123:11014–25.

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