

Cellulose Solubility in Deep Eutectic Solvents: Inspecting Quantitative Hydrogen-Bonding Analysis

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 Electronic Supplementary Information

Abstract According to the Kamlet-Abraham-Taft (KAT) polarity parameters (α , β , π^*), polymers and solvents can be categorized as hydrogen-bond (H-bond) acidic ($\alpha > \beta$) or H-bond basic ($\alpha < \beta$). Recently, we proposed a quantitative hydrogen bonding (QHB) analysis to predict the solubility of polymers in ionic liquids (ILs) using the product of $\Delta\alpha\Delta\beta < 0$ as an indicator, where $\Delta\alpha$ is the difference between the H-bond acidic parameters of the polymer and IL, and $\Delta\beta$ is the difference in their basicity, while the prerequisite of the “complementary” principle (i.e., that one component is H-bond acidic and the other is basic) is satisfied. Here, the applicability of QHB analysis was first confirmed by testing the solubilities of carefully chosen polymer/deep eutectic solvent (DES) pairs, as the DESs were eutectic mixtures dominated by hydrogen bonding interactions. Then, our attention focused on the solubility of cellulose in DESs. Our testing results as well as the typical published results were summarized, which indicate that the potential DESs for cellulose dissolution and regeneration must be of the H-bond basic type because the “complementary” principle should be satisfied as a prerequisite. However, the H-bond basic DESs investigated in this study do not show the superior solubility of cellulose that has been commonly observed for H-bond basic ILs, even if the criterion of $\Delta\alpha\Delta\beta < 0$ is satisfied for both DESs and ILs. Possible reasons for this discrepancy are given to understand the varying effectiveness in cellulose dissolution for H-bond basic DESs and ILs.

Keywords Deep eutectic solvent; Cellulose dissolution; Empirical polarity parameters; Hydrogen bonding interaction

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INTRODUCTION

Polymer dissolution in solvents is always an important area attracting considerable interest from researchers in polymer science and engineering because in many applications, polymers are directly utilized or further modified/processed in the form of solution.^[1–3] Knowledge about the physical chemistry of polymer solutions is also an important theme for the foundation of polymer science.^[4] Currently, many physical parameters of polymers still have to be characterized using their solutions, such as measuring the molecular weight and molecular weight distribution using gel permeation chromatography (GPC) and detecting the branching lever of polyolefins using nuclear magnetic resonance (NMR) spectroscopy.

It is well accepted that Flory-Huggins theory for dilute solutions (Eq. 1) is the cornerstone to understand and predict the solvation process for polymers and the phase behavior of

polymer solutions.^[5] In this theory, the free energy of mixing (ΔG_m) is composed of entropy ($-T\Delta S_m$) and enthalpy (ΔH_m) terms, which is written as follows:

$$\Delta G_m = -T\Delta S_m + \Delta H_m \\ = kT(\phi_s \ln \phi_s + \frac{\phi_p}{N_p} \ln \phi_p) + kT(\chi \phi_p \phi_s) \quad (1)$$

where ϕ_s and ϕ_p are the volume fractions of solvent and polymer, respectively; N_p is the ratio of the molar volume of polymer to that of solvent and is proportional to the degree of polymerization; χ is called the Flory-Huggins interaction parameter, which is proportional to $(\delta_p - \delta_s)^2/RT$, and δ_p and δ_s are the so-called Hildebrand solubility parameters for polymer and solvent, respectively. During the dissolving process for the polymer, the entropy change ($\Delta S_m > 0$) always favors the mixing of the polymer and solvent, but its value is usually small, and the free energy change is mainly controlled by the enthalpy term. An effective interaction parameter χ_{eff} can be adopted to account for the nonideality of real polymer solutions.^[5] When $\chi_{\text{eff}} < 0$, the enthalpy item also favors the dissolution of the polymer in the selected solvent. If there is a way to predict the sign of χ_{eff} , the solubility of a polymer/solvent pair can be forecast.

Recently, we proposed a quantitative hydrogen-bonding

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(QHB) analysis method to access and help to predict the solubility of polymers in room-temperature ionic liquids (ILs).^[6] This method is based on the Kamlet-Abraham-Taft (KAT) polarity parameters, which have been extensively used for characterizing different types of solute/solvent interactions.^[7–9] The KAT polarity parameters in a simplified form of linear solvation energy relationship (LSER) is given by:^[10]

$$(XYZ) = (XYZ)_0 + s\pi^* + a\alpha + b\beta \quad (2)$$

where (XYZ) is the solvent-dependent physico-chemical property determined for a variety of solvents, $(XYZ)_0$ is the same property for a reference medium (e.g., gas phase or inert solvent), α , denoting the hydrogen-bond (H-bond) donating ability or acidity, β , denoting the H-bond accepting ability or basicity, π^* , a mixed parameter representing the polarizability and dipolarity, s , a , and b are solvent-independent coefficients reflecting the related influence of the π^* , α , and β -components, respectively, upon (XYZ) . The polarity parameters, α , β , and π^* , are usually obtained using the so-called solvatochromic comparison method.^[9,11,12] Polymers and ILs can be categorized as either H-bond acidic ($\alpha > \beta$) or H-bond basic ($\alpha < \beta$). First, the “complementary” requirement, i.e., one H-bond acidic component and another basic component, must be fulfilled to dissolve the polymer in a selected IL. Then, if the product of $\Delta\alpha\Delta\beta < 0$, where $\Delta\alpha = \alpha_p - \alpha_{IL}$ and $\Delta\beta = \beta_p - \beta_{IL}$, the IL usually exhibits satisfying solubility for the tested polymer. Strictly speaking, the change of hydrogen bonding interaction energy for the dissolving of polymer in an IL should be $(A\alpha_{IL}\beta_p + B\alpha_p\beta_{IL}) - (C\alpha_p\beta_p + D\alpha_{IL}\beta_{IL})$, where A , B , C and D are coefficients according to Eq. (2).^[10] However, the good correlation of $\Delta\alpha\Delta\beta = -[(\alpha_{IL}\beta_p + \alpha_p\beta_{IL}) - (\alpha_p\beta_p + \alpha_{IL}\beta_{IL})] < 0$ and the solubility of polymer/IL mixtures suggests that the simplified relationship, $(\alpha_{IL}\beta_p + \alpha_p\beta_{IL}) - (\alpha_p\beta_p + \alpha_{IL}\beta_{IL})$, can be used to approximately predict the change of hydrogen bonding interaction energy for the mixing of polymer/IL, i.e., $\Delta\alpha\Delta\beta < 0$ generally indicates that the hydrogen bonding interaction energy between the polymer and IL is higher than the hydrogen bonding interaction energy inside the components themselves. Because nonspecific (van der Waals) and polar interactions are commonly weaker than hydrogen bonding interactions in polymer/IL mixtures, QHB analysis ($\Delta\alpha\Delta\beta$) provides a simple but reliable way to predict the sign of ΔH_m (i.e., χ_{eff}), and thus the solubility of a polymer/IL mixture.

Deep eutectic solvents (DESs) are eutectic mixtures, typically composed of hydrogen bond acceptors (HBAs, e.g., quaternary ammonium salts, and aromatic alcohols) and hydrogen bond donors (HBDs, e.g., carboxylic acids, amides, amines, and polyols) at certain stoichiometric ratios.^[13–15] They are considered as “designer” solvents that are alternatives to ILs because they also exhibit negligible vapor pressures at room temperature, and their physico-chemical properties can be fine-tuned by varying the starting HBA and HBD components or simply altering their molar ratios. They have extra advantages compared with ILs; for example, they do not need any solvent and special purification steps during synthesis, and they usually have low toxicity and cost, as the raw materials for preparation are usually nontoxic and abundant.^[16] DESs, as new-generation solvents, show application potential in many fields of polymer sciences, such as polymer polymerization,^[17] biomass fractionation,^[18] and ion-

ic soft materials.^[19] Most of these applications involve the dissolution of polymers in desired DESs. It is well accepted that hydrogen bonding plays an important role in the depression of melting points for HBA and HBD components and the formation of DESs. On that account, it is believed that the QHB analysis developed for polymer/IL mixtures can also work well for predicting the solubility of polymers in DESs.

Here, the validity of QHB analysis was first evaluated by testing the solubility of carefully selected polymer/DES pairs. Then, attention was given to the solubility of cellulose in DESs because most DESs adopted to dissolve cellulose materials actually show no or very limited solubilities.^[20–22] The QHB analysis based on hydrogen bonding interactions can provide a rational explanation.

RESULTS AND DISCUSSION

Evaluating the Applicability of QHB Analysis for Polymer/DES Mixtures

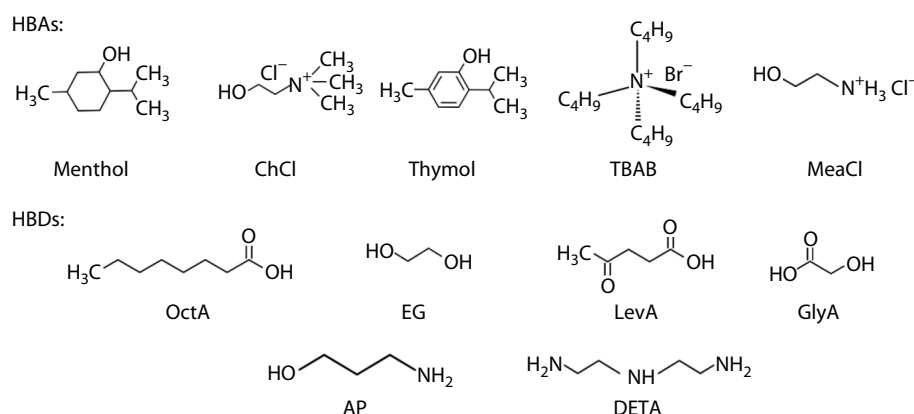
First, the applicability of QHB analysis for polymer/DES mixtures is evaluated by testing the solubilities of seven typical polymers in carefully selected DESs. The details about the polymers used in this study are provided in the electronic supplementary information (ESI). The investigated polymers are listed in Table S1 (in ESI) with the chemical structure and the KAT parameters (α , β , π^*) for each polymer. According to the relative sizes of the α and β values, the seven polymers can be categorized as H-bond basic or H-bond acidic polymers. It should be noted that the α values of H-bond basic polymers are zero or near zero, indicating that there are more electronegative functional groups in these polymers, which commonly act as proton acceptors in forming hydrogen bonds.^[23] Correspondingly, nine DESs are chosen to pair with these polymers to prepare solutions. Similarly, the DESs can also be categorized into H-bond acidic DESs (Nos. 1–4 in Table 1) or basic DESs (Nos. 7–9 in Table 1). Unlike ILs, some DESs have almost the same α and β values that can be called H-bond neutral DESs (Nos. 5 and 6 in Table 1). Noted that the DESs investigated here are all the type III DESs without the component of metal halides,^[13] as there might exist different types of interactions between polymers and metal ions other than hydrogen bonding interaction for the other three types of DESs. Moreover, the DESs are selected mainly based on their α and β values. We try to keep the β values invariant, while make the α values gradually change in a relatively wide range for the selected H-bond acidic and H-bond basic DESs, respectively. The chemical structures of the HBA and HBD components used to synthesize these DESs are given in Fig. 1. The hydrophilicity/hydrophobicity for every DES according to its solubility in water is also provided in Table 1. However, the hydrophilicity/hydrophobicity does not show any distinct influence on the solubilities of the investigated polymer/DES mixtures according to the solubility testing results, as discussed below. The experimental details about the preparation of DESs, and the dissolution conditions of the selected polymers in these DESs can be found in ESI.

Poly(vinyl pyrrolidone) (PVP) possesses the highest β value among the selected H-bond basic polymers (Table S1 in ESI). It can be dissolved by both H-bond acidic and H-bond neutral DESs no matter they are hydrophilic or hydrophobic, but it is insoluble in all the H-bond basic DESs used in this study,

Table 1 The compositions and KAT parameters for DESs used to test the applicability of the QHB analysis method for polymer/DES mixtures.

No.	DES(HBA-HBD) ^a	Molar ratio	α	β	π^*	Hydrophilicity/ Hydrophobicity	Ref.
H-bond acidic							
1	Menthol-OctA	1:1	1.77	0.50	0.41	Hydrophobic	[12]
2	Menthol-LevA	1:1	1.56	0.58	0.66	Hydrophobic	[12]
3	ChCl-EG	1:2	1.47	0.57	1.07	Hydrophilic	[12]
4	Thymol-OctA	1:1	1.10	0.05	0.67	Hydrophobic	[24]
H-bond neutral							
5	ChCl-GlyA	1:2	0.49	0.50	1.08	Hydrophilic	[12]
6	ChCl-LevA	1:2	0.51	0.57	1.00	Hydrophilic	[12]
H-bond basic							
7	TBAB-AP	1:2	0.27	0.88	1.08	Hydrophilic	[25]
8	TBAB-AP	1:4	0.39	0.90	1.02	Hydrophilic	[25]
9	MeaCl-DETA	1:4	0.54	0.90	1.06	Hydrophilic	[25]

^a Names and abbreviations of HBAs and HBDs: choline chloride: ChCl; octoic acid: OctA; levulinic acid: LevA; glycolic acid: GlyA; ethylene glycol: EG; tetrabutylammonium bromide: TBAB; 3-amino-1-propanol: AP; monoethanolammonium chloride: MeaCl; diethylenetriamine: DETA.

**Fig. 1** The chemical structures of the HBA and HBD components used to synthesize the DESs that are listed in Table 1.

even when the criterion of $\Delta\alpha\Delta\beta < 0$ is satisfied (Table S2 in ESI). Two other H-bond basic polymers, polyethylene oxide (PEO) and polyvinyl acetate (PVAc), are also insoluble in the H-bond basic DESs. Additionally, they are not soluble in the selected H-bond neutral DESs. For PVAc, this can be ascribed to both $\Delta\alpha$ and $\Delta\beta$ being less than zero, and the fact that $\Delta\alpha\Delta\beta < 0$ requirement is not satisfied. However, for PEO, its insolubility in the DESs formed by ChCl with GlyA and LevA, respectively, does not satisfy the criterion of $\Delta\alpha\Delta\beta < 0$, as ($\Delta\alpha$, $\Delta\beta$) are (−0.49, 0.15) and (−0.51, 0.08) for two PEO/DES pairs. It can be found that the two $\Delta\beta$ values are relatively small. Considering that the used KAT parameters are adopted from different references and are obtained by using different solvatochromic probes, an uncertainty of 0.1 or even more for KAT parameters is very possible.^[11] This is an unavoidable limitation of the solvatochromic comparison method. The accuracy of the QHB analysis is mainly determined by the accuracy of KAT parameters adopted. As a suggestion, it is better to use KAT parameters measured using the same sets of solvatochromic probes to ensure the predictive accuracy of QHB analysis. Taking the possible uncertainties of KAT parameters into account, the insolubility of PEO in these two solvents is acceptable even as the QHB analysis predicts the solubility. On the other hand, for all the tested H-bond acidic polymer/H-bond acidic DES pairs, none are soluble regardless of whether or not the criterion of $\Delta\alpha\Delta\beta < 0$ is satisfied. All these results suggest that the “complementary” principle of solubility (one

component H-bond acidic and the other basic) we have previously found in polymer/IL mixtures^[6] is also well applicable for the polymer/DES mixtures studied here, while the H-bond neutral DESs can be considered to exhibit duality, *i.e.*, they can be treated as either H-bond acidic or H-bond basic.

For all 13 pairs of H-bond basic polymer/H-bond acidic DES examined here (Table S2 in ESI), only two pairs violate the proposed $\Delta\alpha\Delta\beta$ criterion. One is PEO/ChCl-EG (insoluble), and the other is PVAc/menthol-LevA (soluble). The values of ($\Delta\alpha$, $\Delta\beta$) for the two mixtures are (−1.47, 0.08) (soluble as predicted) and (−1.56, −0.18) (insoluble as predicted), respectively. The failure to predict solubility can also be ascribed to the uncertainty in the adopted KAT parameters.

When we tried to seek H-bond basic DESs, it was found that they are evidently less than the H-bond acidic DESs. In a typical DES, the molar percentage of the HBD component is commonly equal to or higher than that of HBA. Moreover, the HBA component is usually an organic salt, which can also be considered to be composed of HBA (anion) and HBD (cation) components. Thus, there are more functional groups inside a DES that can play the role of proton donors, and thus, it is prone to exhibit as H-bond acidic, which embodies a relatively high α value. Although some research works have been carried out to systemically study the influence of the types, chemical structures, and molar ratios of HBA and HBD on the polarities of different families of DESs, a general and detailed delineation has not been obtained at present.^[12,26–28]

The synthetic H-bond acidic polymers tested here, poly(vinyl alcohol) (PVA) and poly(2-hydroxyethyl methacrylate) (PHEMA), can be easily dissolved by H-bond basic DESs (dissolved polymer concentration ≥ 2.0 wt%) when the criterion of $\Delta\alpha\Delta\beta < 0$ is well met. For microcrystalline cellulose (MCC), the situation is quite different. It is well known that cellulose is difficult to dissolve due to the strong intra- and inter-molecular interactions between cellulose chains and the resulting high degree of crystallinity.^[29] Both the high α (1.31) and β (0.62) values of MCC suggest the strength of the hydrogen bonding interactions inside cellulose macromolecules. For the three H-bond basic DESs listed in Table 1, only the DES of MeaCl-DETA (1:4) shows a distinct dissolving capacity for MCC. It can dissolve more than 2.0 wt% MCC after being heated at 110 °C for 24 h. Less than 0.2 wt% MCC can be dissolved by the other two TBAB-based DESs under the same conditions, although they should have considerable dissolving ability according to the ($\Delta\alpha$, $\Delta\beta$) values obtained for mixtures of MCC and TBAB-based DESs (Table S2 in ESI). More discussions about the solubility of cellulose in various DESs will be given in the next section.

The solubility and the corresponding ($\Delta\alpha$, $\Delta\beta$) values for all the tested polymer/DES pairs listed in Table S2 (in ESI), which satisfy the “complementary” requirement, are depicted in the $\Delta\beta$ - $\Delta\alpha$ coordinate system (Fig. 2) as we have done previously for polymer/IL mixtures.^[6] There should be four kinds of situations according to the combinations of solubility/insolubility and positive/negative $\Delta\alpha\Delta\beta$ values. The soluble polymer/DES mixtures appear in the second and fourth quadrants when the criterion of $\Delta\alpha\Delta\beta < 0$ is fulfilled. Due to the relatively high α values of DESs, there is no insoluble polymer/DES pair, which satisfies the “complementary” principle and simultaneously shows both positive $\Delta\alpha$ and $\Delta\beta$ val-

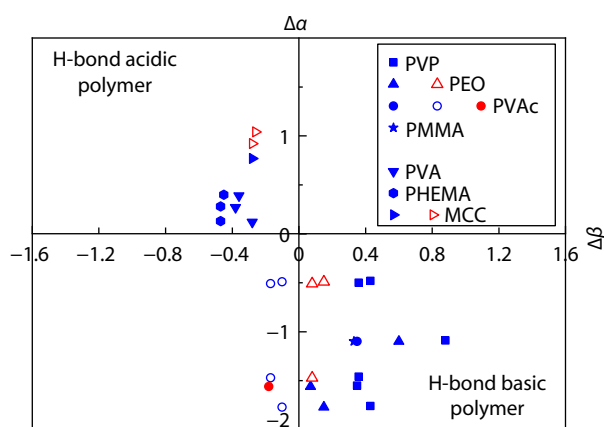


Fig. 2 The experimentally obtained solubilities compared with the predicted results based on QHB analysis ($\Delta\alpha\Delta\beta$) for all tested polymer/DES pairs depicted in the $\Delta\beta$ - $\Delta\alpha$ coordinate system. The tested mixtures that do not satisfy the “complementary” requirement are not displayed here. There are four kinds of situations according to the combinations of solubility/insolubility and positive/negative $\Delta\alpha\Delta\beta$ values. They are presented with solid (hollow) symbols in blue color and solid (hollow) symbols in red color; the solid (hollow) symbols indicate the soluble (insoluble) situation in actual dissolution experiments, and the blue (red) color denotes the experimentally obtained solubilities agreeing (not agreeing) with the predicted results based on $\Delta\alpha\Delta\beta$.

ues. Thus, there are no polymer/DES data in the first quadrant. The polymer/DES pairs with both negative $\Delta\alpha$ and $\Delta\beta$ values, which appear in the third quadrant, are all H-bond basic polymer/acidic DES mixtures. They should be insoluble, with the only exception being PVAc/Menthol-LevA (−1.56, −0.18). Based on the results presented in Fig. 2 and Table S2 (in ESI), it is confident to say that the QHB analysis based on hydrogen bonding interactions between solute and solvent also works well for justifying or predicting the solubility of polymers in the DESs of type III investigated in this study. More experimental works are needed to verify that whether the QHB analysis is applicable to the dissolution of polymers in the other three types of DESs or not.

Solubilities of Cellulose in DESs

Looking for solvents for cellulose is an important task in the fields of research and application of cellulose because cellulose materials usually have to be dissolved for characterization, modification, and processing.^[3,30,31] A successful solvent or solvent system should be able to effectively break the strong intra- and inter-molecular hydrogen bonding interactions in cellulose. For the KAT parameters of cellulose, both the α (1.31) and β (0.62) values are very high, and $\alpha > \beta$ at the same time. According to the criterion of $\Delta\alpha\Delta\beta < 0$, the potential solvents should be strong H-bond basic solvents with β values larger than that of cellulose.

In the past, many studies have been carried out to develop and evaluate efficient DES solvents for cellulose and to scrutinize the dissolution mechanism.^[20,21,32,33] However, most DESs adopted in these studies are indeed H-bond acidic DESs, which show no or very limited solubility for cellulose materials, as listed in the upper part of Table 2, including many ChCl-based DESs reported in the literature.

We also selected four H-bond acidic DESs to test their dissolving capacities for MCC (c.f., Table 1 and Table S2 in ESI). There was no sign of the dissolution of MCC with a concentration of 0.2 wt% in these DESs after the MCC/DES mixtures were heated at 110 °C for 24 h. The white MCC powders in the mixtures settled down very quickly to the bottom of the glass bottles after the stirring was stopped (Fig. S1 in ESI). Moreover, the light-yellow colors observed for some mixtures, such as those in Figs. S1(b) and S1(d) (in ESI), are due to the solvents themselves and are not caused by the long-time heating or dissolution of cellulose.

TBAB-AP, as a kind of H-bond basic DES, were picked to study their dissolving capacity for H-bond acidic polymers. PVA and PHEMA showed good solubilities (≥ 2.0 wt%) in TBAB-AP DESs with molar ratios of both 1:2 and 1:4, which conformed to the prediction of QHB analysis very well. However, MCC with a concentration of 0.2 wt% was only partially dissolved in both solvents even after being heated at 110 °C for 24 h (Figs. 3a and 3b). The mixture of 0.2 wt% MCC/TBAB-AP (1:4) was observed using a polarized optical microscope (POM) before and after heating (Fig. S2 in ESI). It is obvious that most of the crystallized MCC particles disappear, but bright dots or areas are still observed indicating the insoluble particles. The photos verify that MCC can be partially dissolved in TBAB-AP (1:4). The results obtained from POM observation are similar to those obtained for the other three DESs based on tetrabutylammonium halite listed in Fig. 3.

Table 2 Summary of KAT parameters of some typical DESs and ILs used to dissolve cellulose and the corresponding solubility.

DESs							
HBA ^a	HBD ^a	Molar ratio	α	β	π^*	Solubility	Ref.
H-bond acidic DESs							
ChCl	EG	1:2	1.47	0.57	1.07	No ^c	[20]
						~0.05 wt% ^d	[21]
	Gly	1:2	1.49 ^[12]	0.52	1.11	No ^e	This work
						No ^c	[20]
	1,3-Propanediol	1:2	—	—	—	~0.01 wt% ^d	[21]
						No ^c	[20]
	1,5-Pentanediol	1:3.5	—	—	—	~0.04 wt% ^d	[21]
						No ^c	[20]
	Urea	1:2	1.42 ^[12]	0.50	1.14	No ^c	[20]
						~0.01 wt% ^d	[21]
Menthol	LacA	1:2	1.335 ^[35]	0.503	0.852	No ^f	[34]
						No ^c	[20]
	OxaA	1:2	1.90 ^[36]	0.41	—	~0.03 wt% ^d	[21]
						No ^e	This work
Thymol	OctA	1:1	1.77	0.50	0.41	No ^e	This work
						LevA	1:1
TBACl	OctA	1:2	1.10	0.05	0.67	No ^e	This work
						1.41 ^[12] (0.84) ^[37]	0.99(1.19)
H-bond basic DESs							
ChCl	Im	3:7	—	0.864 ^[32]	0.382	2.48 wt% ^g	[32]
						No ^f	[34]
ChOH	Urea	1:2	0.72 ^[34]	1.88	1.32	9.51 wt% ^h	[34]
TBACl	AP	1:2	—	—	—	<0.2 wt% ^e	This work
		1:4	—	—	—	<0.2 wt% ^e	This work
TBAB	AP	1:2	0.27	0.88	1.08	<0.2 wt% ^e	This work
		1:4	0.39	0.90	1.02	<0.2 wt% ^e	This work
MeaCl	DETA	1:2	—	—	—	<0.2 wt% ^e	This work
		1:4	0.54	0.90	1.06	2.0 wt%—3.0 wt% ^e	This work
H-bond basic ILs ^b							
	[C ₄ mim][Cl]		0.45 ^[6]	0.83	1.09	25 wt% ⁱ	[38]
	[C ₇ mim][OAc]		0.51 ^[6]	0.99	1.08	25 wt% ^j	[39]

^a Name and abbreviation of HBAs and HBDs (those provided in Table 1 are not repeated here): glycerol: Gly; lactic acid: LacA; oxalic acid dihydrate: OxaA; tetrabutylammonium chloride: TBACl; choline hydroxide: ChOH; imidazole: Im; ^b Name and abbreviation of ILs: 1-butyl-3-methylimidazolium chloride: [C₄mim][Cl]; 1-ethyl-3-methylimidazolium acetate: [C₂mim][OAc]; ^c MCC or α -cellulose powder; heated from 30.0 °C to 100.0 °C at 1 °C·min⁻¹; ^d M_w of cellulose: 8.74×10^4 ; magnetically stirred at 25 °C for at least one week; ^e MCC, average degree of polymerization (DP): ~220; magnetically stirred at 110 °C for 24 h; ^f MCC, DP: 145; heated at 100 °C for 24 h; ^g Cotton lint pulp, DP: ~576; activated by ultrasonic-assisted saturated CaCl₂ solution prior to dissolution; heated at 120 °C for 1.5 h; ^h MCC, DP: 145; heated at 70 °C for 20 minutes; ⁱ Pulp, DP: 1000; microwave heating; ^j MCC, DP: 220; heated at 80 °C.

As chloride anions can form stronger hydrogen bonds with the proton donors than bromide anions, we further prepared TBACl-AP DESs with molar ratios of both 1:2 and 1:4 (Table 2) to determine the influence of varying the anion of the HBA component. However, 0.2 wt% MCC could not be completely dissolved in TBACl-AP DESs either. All the solutions were opaque and had somewhat light-yellow colors, and their viscosities increased evidently. As shown in Fig. 3, the unsolved but swollen MCC particles were suspended in the solvents and did not settle after the magnetic stirring was stopped. The as-prepared DESs were observed to be transparent and colorless, so it was conjectured that the colors of MCC solutions are due to the dissolution of cellulose. The DESs with a molar ratio of 1:4 are more capable of dissolving cellulose than the corresponding DESs with a molar ratio of 1:2, as the yellow colors are slightly deeper for the former (Fig. 3b versus Fig. 3a for TBAB-AP, and Fig. 3d versus Fig. 3c for TBACl-AP).

We further changed the HBD component of TBACl-AP (1:2) from AP to OctA to study the influence of the HBD type on the dissolving capacity of cellulose. This solvent attracted our attention because it has two sets of KAT parameters in the literature, (1.41, 0.99, 0.76)^[12] versus (0.84, 1.19, 0.80)^[37] which

indicates that it is either H-bond acidic or basic. Its mixture with 0.2 wt% MCC exhibits a very similar appearance to that of other H-bond acidic DESs in dissolving MCC. The MCC powders were not dissolved, and they also settled at the bottom of the solvent after thermal dissolution was stopped (Fig. S1e, in ESI). This result indicates that TBACl-OctA (1:2) is indeed a H-bond acidic DES. This is reasonable considering the difference in hydrogen bond donating abilities between AP and OctA.^[12]

The DESs formed by MeaCl (HBA) and DETA (HBD) were another type of H-bond basic DESs that we used to dissolve the H-bond acidic polymers. When the molar ratio of MeaCl and DETA is 1:2, MCC with a concentration of 0.2 wt% cannot be completely dissolved, and the mixture exhibits a similar appearance as that for mixtures formed with the DESs based on tetrabutylammonium halite, as shown in Fig. 3. When the molar ratio of MeaCl and DETA changes to 1:4, 2.0 wt% cellulose could be completely thermally dissolved (110 °C, 24 h), and a transparent solution with a light-yellow color can finally be obtained. The dissolution of cellulose could be verified by observing the mixture using POM before and after thermal dissolution, as the cellulose crystals were observed to

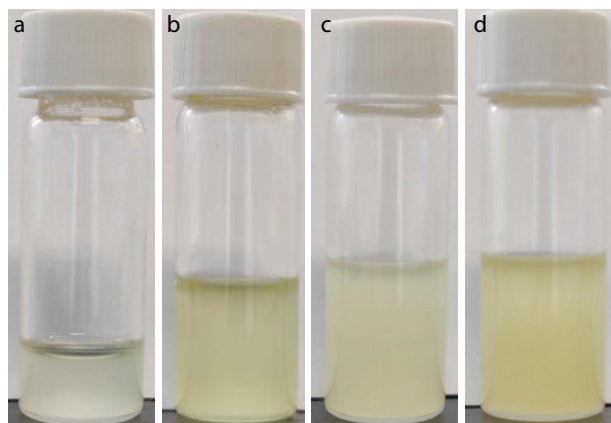


Fig. 3 Photographs of the mixtures of MCC and different H-bond basic DESs composed of tetrabutylammonium halite and 3-amino-1-propanol (AP): (a) TBAB-AP (1:2), (b) TBAB-AP (1:4), (c) TBACl-AP (1:2), and (d) TBACl-AP (1:4). The concentration of MCC in the mixtures is 0.2 wt%. MCC is partially dissolved in these solvents after being heated at 110 °C for 24 h.

completely disappear, and the field of vision under polarized light was observed to be completely dark for the obtained solution at 80 °C (Fig. 4). The solution was observed at high temperature because we found that a transparent solution was obtained if it was naturally cooled to room temperature without any external disturbance. However, if the solution was slightly disturbed during cooling, such as gently hand-stirring with a steel bar for tens of seconds, the dissolved cellulose chains could crystallize with the solvent molecules, forming rod-like crystals, as shown in the optical micrograph (Fig. S3 in ESI). The rod-like crystals could be fully melted upon heating for 5 min at 80 °C.

The MCC concentration was further increased to 3.0 wt%, and an almost transparent solution could be obtained under the same dissolving conditions. However, scattered bright areas or dots could be observed in the optical micrograph obtained at room temperature under polarized light (Fig. S4b in ESI). The density of bright dots was gradually decreased as the temperature reached 80 °C and stayed constant for several minutes at this temperature (Figs. S4c and S4d in ESI), but the bright dots did not totally disappear as the heating time was extended. These observations indicate that the upper limit of solubility of MCC for MeaCl-DETA (1:4) is slightly less

than 3.0 wt%. Moreover, the crystallization of dissolved cellulose chains with DES molecules was not so obvious for the 3.0 wt% MCC solution. This led us to hypothesize that this cocrystallization process is most likely a diffusion-controlled process because the viscosity of the 3.0 wt% MCC solution is evidently higher than that of the 2.0 wt% solution.

Similarities and Differences between the Dissolution of Cellulose in DESs and ILs

The survey carried out here and other typical published results for investigating the solubilities of cellulose in different DESs and ILs, including the dissolving conditions used, are summarized in Table 2. The KAT parameters for all solvents are collected, and they are categorized as H-bond acidic or basic according to the size of the α and β values. According to all the results summarized in Table 2, it can be said that the potential solvents for cellulose dissolution and regeneration must be H-bond basic solvents for both DESs and ILs because the “complementary” principle, as a prerequisite, should be satisfied.

Moreover, the ILs that fulfil the criterion of $\Delta\alpha\Delta\beta < 0$ commonly show the superior solubility of cellulose (≥ 10 wt%),^[38,39] but the capacities for dissolving cellulose for H-bond basic DESs are not as high even though the $\Delta\alpha\Delta\beta < 0$ criterion is satisfied. For the six H-bond basic DESs investigated here (Table 2), only the DES of MeaCl-DETA (1:4) displays an acceptable solubility of MCC between 2 wt% and 3 wt%. In the literature, it is also rare to find H-bond basic DESs prepared with the most common HBAs and HBDs showing excellent solubility for cellulose materials.^[33,34] There are two possible reasons for this difference. First, there are fewer ions or functional groups for DESs that can act as HBAs to form hydrogen bonds with —OH groups of the sugar units of cellulose, which is believed to play an important role in weakening the hydrogen bonding interactions in cellulose crystals and enhancing its dissolution. The molecular dynamics (MD) simulation results also suggest that the number of hydrogen bonds formed between cellulose-DESs is less than that between cellulose-ILs.^[22,40] The second reason, as suggested by Abbott *et al.*,^[21] is that ILs usually have a more ordered microstructure compared to DESs; thus, the entropy gain is higher for the dissolution of cellulose in ILs compared to the dissolving process in DESs. However, we think this reason should be a minor influencing factor because the free energy of solvation is mainly controlled by the enthalpy part for the

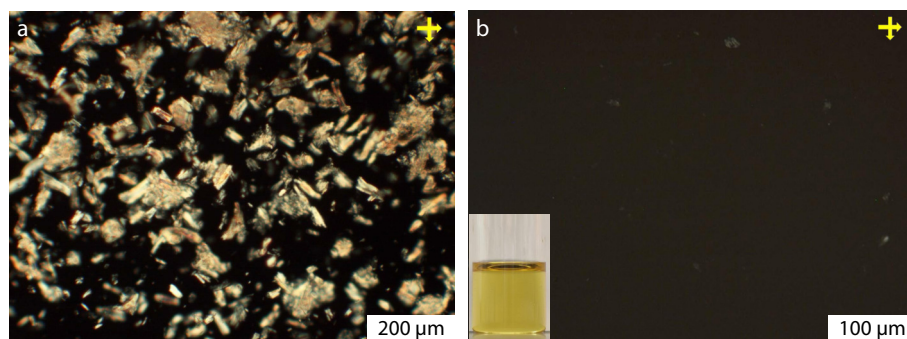


Fig. 4 POM images of (a) 2.0 wt% MCC/MeaCl-DETA (1:4) mixture before thermal dissolution, and (b) the as-obtained solution heated at 80 °C for 5 min using a hot-stage attached to the optical microscope. The inset of (b) shows the appearance of a 2.0 wt% MCC/MeaCl-DETA (1:4) solution.

dissolving process.

In addition, the type and molar ratio of HBA and HBD for DESs can be varied to fine-tune their physico-chemical properties. These strategies were also used to study their influences on the solubilities of cellulose for the H-bond basic DESs investigated in this study. Among all the variable factors, the HBA to HBD molar ratio showed an apparent influence on their solubility for cellulose, which was especially obvious for the DES of MeaCl-DETA. MCC could be dissolved in MeaCl-DETA (1:4) with a concentration ≥ 2.0 wt%, while 0.2 wt% MCC could not be totally dissolved using MeaCl-DETA (1:2). This was unexpected because a change in the molar ratio of HBA and HBD generally did not show much influence on the polarity properties of DESs.^[12] The unanticipated result suggests that at least for the MeaCl-DETA system, the HBD component DETA plays a positive role in enhancing the dissolution of cellulose. More experimental works as well as theoretical calculations are needed to explore in the future to understand the influence of complex hydrogen bonding interactions between HBD and HBA in a DES and between cellulose and HBD of a DES on the dissolution of cellulose.

Additionally, it is worth noting that cellulose/IL solutions and many synthetic polymer/IL solutions usually show concentration-dependent indices for the specific viscosity (η_{sp}) of 1, 2, and 14/3 in dilute, semi-dilute, and concentrated regimes, respectively, which is the power law for a neutral polymer in θ -solvent, as predicted by the scaling theory.^[41] Recently, Liu *et al.* reported that for the solutions of cellulose/DES of choline hydroxide (ChOH)-urea (1:2), the scaling values were 0.54, 1.47, and 3.21 in three regimes, which closely follow the power laws of 1/2, 3/2, and 15/4 obtained for salt-free polyelectrolyte solutions.^[34] It should be noted that the ChOH-urea DES used to prepare cellulose solutions is an aqueous system with a water content of 11.8 wt%. The upper limit of solvability of cellulose for MeaCl-DETA (1:4) DES is < 3.0 wt%, so we did not measure the scaling relationship of $\eta_{sp} \sim c$ for its cellulose solutions, as not enough data points would be available in the concentrated regimes. Instead, we measured the scaling relationships for the solutions of PMMA/Thymo-OctA (1:1), as Thymol-OctA (1:1) showed a superior solubility for PMMA. The $\eta_{sp} \sim c$ scaling relationships for the PMMA/Thymol-OctA solutions are 1.05, 1.85, and 3.87 (Fig. S5 in ESI), which are close to the power laws of 1.0, 1.3, and 3.9 obtained for the neutral polymer in a good solvent.^[42] Moreover, the ratio between entanglement concentration, c_e , and overlap concentration, c^* , of PMMA/Thymol-OctA solutions is ~ 10 (Fig. S5 in ESI), and this is an important feature for polymer solutions in good solvents.^[42,43] It has been realized that ILs are more dynamically heterogeneous than DESs with similar functionalities, which are due to the display of different intermolecular interactions within the constituent species.^[44] The different solution dynamics between polymer/IL and polymer/DES also point to the fact that different heterogeneous microstructures and dynamics might exist in the two kinds of solutions. More experimental results are needed to explore this topic in the future.

CONCLUSIONS

The applicability of the newly developed QHB analysis based on the KAT polarity parameters for polymer/DES (the type III)

was evaluated by testing the solubility of carefully selected polymer/DES pairs. The DES systems were chosen because it was generally accepted that hydrogen bonding interactions play an important role in the formation of DESs. Based on the dissolution results for all the tested polymer/DES pairs, it is concluded that (1) the “complementary” principle (one component H-bond acidic and the other basic) as a prerequisite has to be satisfied if a polymer can be expected to be dissolved in a desired DES. The “complementary” principle can help one to understand why many DESs exhibit very limited or no solubilities for cellulose materials in previous studies. This is because most of the DESs adopted in these studies have been of the H-bond acidic type. It is not surprising that cellulose, which is a kind of strong H-bond acidic polymer, cannot be dissolved in H-bond acidic DESs. (2) The QHB analysis works well for predicting the solubility of polymers in DESs. The H-bond basic DESs, which satisfy the criterion of $\Delta\alpha\Delta\beta < 0$, exhibit positive capacities for cellulose dissolution. The DES of MeaCl-DETA (1:4) can dissolve MCC at concentrations ranging between 2.0 wt% and 3.0 wt%. However, the superior solubility of cellulose (≥ 10 wt%), which is very common for typical H-bond basic ILs, is rarely observed for H-bond basic DESs. Two possible reasons for this are proposed: the number of hydrogen bonds formed between cellulose-DESs is less than that between cellulose-ILs, and the entropy gain for the dissolution of cellulose in ILs is higher than that for the dissolution process in DESs.

In the future, more research is needed to delineate the influences of the types, chemical structures, and molar ratios of HBA and HBD species on the KAT polarities of DESs. The first-principle-based COSMO-RS derived modeling approach has also been used to predict the KAT polarity scales of DESs.^[45] It is believed that all these efforts will help to rapidly screen efficient DESs with the guidance of QHB analysis for the dissolution of a specific polymer, including natural polymers, such as cellulose, lignin, chitin, and starch.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2801-6>.

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REFERENCES

- 1 Brem, A.; Lhost, O.; Tervoort, T. A. Influence of solvent quality and crystallization conditions on the drawability of ultra-high

- molecular weight polyethylene cast from solution. *Macromolecules* **2020**, *53*, 5957–5970.
- 2 Pereira, R. F. P.; Brito-Pereira, R.; Goncalves, R.; Silva, M. P.; Costa, C. M.; Silva, M. M.; Bermudez, V. D.; Lanceros-Mendez, S. Silk fibroin separators: a step toward lithium-ion batteries with enhanced sustainability. *ACS Appl. Mater. Interfaces* **2018**, *10*, 5385–5394.
 - 3 Zhang, J. M.; Wu, J.; Yu, J.; Zhang, X. C.; Mi, Q. Y.; Zhang, J. Processing and functionalization of cellulose with ionic liquids. *Acta Polymerica Sinica* (in Chinese) **2017**, 1058–1072.
 - 4 Flory, P. J., *Principles of Polymer Chemistry*, Cornell University Press, New York, **1953**.
 - 5 Hiemenz, P. C.; Lodge, T. P., Chapter 7 in *Polymer Chemistry*, 2nd Edition, CRC Press, New York, **2007**.
 - 6 Yuan, Y. F.; Zhang, J. M.; Zhang, B. Q.; Liu, J. J.; Zhou, Y.; Du, M. X.; Han, L. X.; Xu, K. J.; Qiao, X.; Liu, C. Y. Polymer solubility in ionic liquids: dominated by hydrogen bonding. *Phys. Chem. Chem. Phys.* **2021**, *23*, 21893–21900.
 - 7 Kamlet, M. J.; Abboud, J. L. M.; Abraham, M. H.; Taft, R. W. Linear solvation energy relationships. 23. A comprehensive collection of the solvatochromic parameters π^* , α , and β , and some methods for simplifying the generalized solvatochromic equation. *J. Org. Chem.* **1983**, *48*, 2877–2887.
 - 8 Abraham, M. H. Scales of solute hydrogen-bonding: their construction and application to physicochemical and biochemical processes. *Chem. Soc. Rev.* **1993**, *22*, 73–83.
 - 9 Reichardt, C. Polarity of ionic liquids determined empirically by means of solvatochromic pyridinium *N*-phenolate betaine dyes. *Green Chem.* **2005**, *7*, 339–351.
 - 10 Spange, S.; Reuter, A.; Vilsmeier, E.; Heinze, T.; Keutel, D.; Linert, W. Determination of empirical polarity parameters of the cellulose solvent *N,N*-dimethylacetamide/LiCl by means of the solvatochromic technique. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1945–1955.
 - 11 Ab Rani, M. A.; Brant, A.; Crowhurst, L.; Dolan, A.; Lui, M.; Hassan, N. H.; Hallett, J. P.; Hunt, P. A.; Niedermeyer, H.; Perez-Arlandis, J. M.; Schrems, M.; Welton, T.; Wilding, R. Understanding the polarity of ionic liquids. *Phys. Chem. Chem. Phys.* **2011**, *13*, 16831–16840.
 - 12 Florindo, C.; McIntosh, A. J. S.; Welton, T.; Branco, L. C.; Marrucho, I. M. A closer look into deep eutectic solvents: exploring intermolecular interactions using solvatochromic probes. *Phys. Chem. Chem. Phys.* **2018**, *20*, 206–213.
 - 13 Smith, E. L.; Abbott, A. P.; Ryder, K. S. Deep eutectic solvents (DESs) and their applications. *Chem. Rev.* **2014**, *114*, 11060–11082.
 - 14 Hansen, B. B.; Spittle, S.; Chen, B.; Poe, D.; Zhang, Y.; Klein, J. M.; Horton, A.; Adhikari, L.; Zelovich, T.; Doherty, B. W.; Gurkan, B.; Maginn, E. J.; Ragauskas, A.; Dadmun, M.; Zawodzinski, T. A.; Baker, G. A.; Tuckerman, M. E.; Savinell, R. F.; Sangoro, J. R. Deep eutectic solvents: a review of fundamentals and applications. *Chem. Rev.* **2021**, *121*, 1232–1285.
 - 15 Ramon, D. J.; Guillena, G., *Deep eutectic solvents: synthesis, properties, and applications*, Wiley-VCH, Weinheim, Germany, **2020**.
 - 16 Plotka-Wasyłka, J.; de la Guardia, M.; Andruch, V.; Vilkova, M. Deep eutectic solvents vs ionic liquids: similarities and differences. *Microchem. J.* **2020**, *159*, 105539.
 - 17 Jablonsky, M.; Skulcova, A.; Sima, J. Use of deep eutectic solvents in polymer chemistry—a review. *Molecules* **2019**, *24*, 3978.
 - 18 Wang, C. G.; Yang, S. Q.; Song, X. B.; Pi, Q. F.; Zhang, Q.; Liu, Q. Y.; Xu, Y.; Chen, L. G.; Ma, L. L. Novel solvent systems for biomass fractionation based on hydrogen-bond interaction: a minireview. *Adv. Sustain. Syst.* **2020**, *4*, 2000085.
 - 19 Tome, L. C.; Mecerreyes, D. Emerging ionic soft materials based on deep eutectic solvents. *J. Phys. Chem. B* **2020**, *124*, 8465–8478.
 - 20 Sosa, F. H. B.; Dias, R. M.; Lopes, A. M. D.; Coutinho, J. A. P.; da Costa, M. C. Fast and efficient method to evaluate the potential of eutectic solvents to dissolve lignocellulosic components. *Sustainability* **2020**, *12*, 3358.
 - 21 Hakkinen, R.; Abbott, A. Solvation of carbohydrates in five choline chloride-based deep eutectic solvents and the implication for cellulose solubility. *Green Chem.* **2019**, *21*, 4673–4682.
 - 22 Alizadeh, V.; Kirchner, B. Molecular level insight into the solvation of cellulose in deep eutectic solvents. *J. Chem. Phys.* **2021**, *155*, 084501.
 - 23 Arunan, E.; Desiraju, G. R.; Klein, R. A.; Sadlej, J.; Scheiner, S.; Alkorta, I.; Clary, D. C.; Crabtree, R. H.; Dannenberg, J. J.; Hobza, P.; Kjaergaard, H. G.; Legon, A. C.; Mennucci, B.; Nesbitt, D. J. Defining the hydrogen bond: an account (IUPAC Technical Report). *Pure Appl. Chem.* **2011**, *83*, 1619–1636.
 - 24 Martins, M. A. R.; Crespo, E. A.; Pontes, P. V. A.; Silva, L. P.; Bulow, M.; Maximo, G. J.; Batista, E. A. C.; Held, C.; Pinho, S. P.; Coutinho, J. A. P. Tunable hydrophobic eutectic solvents based on terpenes and monocarboxylic acids. *ACS Sustain. Chem. Eng.* **2018**, *6*, 8836–8846.
 - 25 Shukla, S. K.; Mikkola, J. P. Intermolecular interactions upon carbon dioxide capture in deep-eutectic solvents. *Phys. Chem. Chem. Phys.* **2018**, *20*, 24591–24601.
 - 26 Farooq, M. Q.; Odugbesi, G. A.; Abbasi, N. M.; Anderson, J. L. Elucidating the role of hydrogen bond donor and acceptor on solvation in deep eutectic solvents formed by ammonium/phosphonium salts and carboxylic acids. *ACS Sustain. Chem. Eng.* **2020**, *8*, 18286–18296.
 - 27 Abbasi, N. M.; Farooq, M. Q.; Anderson, J. L. Investigating the variation in solvation interactions of choline chloride-based deep eutectic solvents formed using different hydrogen bond donors. *ACS Sustain. Chem. Eng.* **2021**, *9*, 11970–11980.
 - 28 Abbasi, N. M.; Farooq, M. Q.; Anderson, J. L. Modulating solvation interactions of deep eutectic solvents formed by ammonium salts and carboxylic acids through varying the molar ratio of hydrogen bond donor and acceptor. *J. Chromatogr. A* **2021**, *1643*, 462011.
 - 29 Ghasemi, M.; Tsiannou, M.; Alexandridis, P. Assessment of solvents for cellulose dissolution. *Bioresour. Technol.* **2017**, *228*, 330–338.
 - 30 Ge, W. J.; Shuai, J. B.; Wang, Y. Y.; Zhou, Y. X.; Wang, X. H. Progress on chemical modification of cellulose in “green” solvents. *Polym. Chem.* **2022**, *13*, 359–372.
 - 31 Zhou, Y.; Zhang, X. C.; Zhang, J. M.; Cheng, Y. H.; Wu, J.; Yu, J.; Zhang, J. Molecular weight characterization of cellulose using ionic liquids. *Polym. Test* **2021**, *93*, 106985.
 - 32 Ren, H. W.; Chen, C. M.; Wang, Q. H.; Zhao, D. S.; Guo, S. H. The properties of choline chloride-based deep eutectic solvents and their performance in the dissolution of cellulose. *BioResources* **2016**, *11*, 5435–5451.
 - 33 Chen, Y. L.; Zhang, X.; You, T. T.; Xu, F. Deep eutectic solvents (DESs) for cellulose dissolution: a mini-review. *Cellulose* **2019**, *26*, 205–213.
 - 34 Zhong, Y. L.; Wu, J. W.; Kang, H. L.; Liu, R. G. Choline hydroxide based deep eutectic solvent for dissolving cellulose. *Green Chem.* **2022**, *24*, 2464–2475.
 - 35 Liu, Q. L.; Zhao, X. H.; Yu, D. K.; Yu, H. T.; Zhang, Y. B.; Xue, Z. M.; Mu, T. C. Novel deep eutectic solvents with different functional groups towards highly efficient dissolution of lignin. *Green Chem.* **2019**, *21*, 5291–5297.
 - 36 Ma, Y.; Xia, Q. Q.; Liu, Y. Z.; Chen, W. S.; Liu, S. X.; Wang, Q. W.; Liu, Y. X.; Li, J.; Yu, H. P. Production of nanocellulose using hydrated deep eutectic solvent combined with ultrasonic treatment. *ACS Omega* **2019**, *4*, 8539–8547.
 - 37 Teles, A. R. R.; Capela, E. V.; Carmo, R. S.; Coutinho, J. A. P.

- Silvestre, A. J. D.; Freire, M. G. Solvatochromic parameters of deep eutectic solvents formed by ammonium-based salts and carboxylic acids. *Fluid Phase Equilib.* **2017**, *448*, 15–21.
- 38 Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. Dissolution of cellulose with ionic liquids. *J. Am. Chem. Soc.* **2002**, *124*, 4974–4975.
- 39 Zhang, J. M.; Xu, L. L.; Yu, J.; Wu, J.; Zhang, X. Y.; He, J. S.; Zhang, J. Understanding cellulose dissolution: effect of the cation and anion structure of ionic liquids on the solubility of cellulose. *Sci. China-Chem.* **2016**, *59*, 1421–1429.
- 40 Brehm, M.; Radicke, J.; Pulst, M.; Shaabani, F.; Sebastiani, D.; Kressler, J. Dissolving cellulose in 1,2,3-triazolium- and imidazolium-based ionic liquids with aromatic anions. *Molecules* **2020**, *25*, 3539.
- 41 Liu, F. Y.; Lv, Y. X.; Liu, J. J.; Yan, Z. C.; Zhang, B. Q.; Zhang, J.; He, J. S.; Liu, C. Y. Crystallization and rheology of poly(ethylene oxide) in imidazolium ionic liquids. *Macromolecules* **2016**, *49*, 6106–6115.
- 42 Colby, R. H. Structure and linear viscoelasticity of flexible polymer solutions: comparison of polyelectrolyte and neutral polymer solutions. *Rheol. Acta* **2010**, *49*, 425–442.
- 43 Graessley, W. W. Polymer chain dimensions and the dependence of viscoelastic properties on concentration, molecular weight and solvent power. *Polymer* **1980**, *21*, 258–262.
- 44 Barik, S.; Chakraborty, M.; Mahapatra, A.; Sarkar, M. Choline chloride and ethylene glycol based deep eutectic solvent (DES) versus hydroxyl functionalized room temperature ionic liquids (RTILs): assessing the differences in microscopic behaviour between the DES and RTILs. *Phys. Chem. Chem. Phys.* **2022**, *24*, 7093–7106.
- 45 Kundu, D.; Rao, P. S.; Banerjee, T. First-principles prediction of Kamlet-Taft solvatochromic parameters of deep eutectic solvent using the COSMO-RS Model. *Ind. Eng. Chem. Res.* **2020**, *59*, 11329–11339.