Supporting Information

Prediction of Solubility Parameters of Lignin and Ionic Liquids Using Multi-resolution Simulation Approaches

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1. Prediction of Eutectic Point Composition of mDES

To confirm the prepared molar ratio of mDES (HBA ($ZnCl_2$) to HBD (ethylene glycol and glycerol)), a method has been formulated to predict the molar ratios using COSMO-RS model. The COSMO-RS model allows calculation of the activity coefficient of any compound in the mixture without any experimental data. The calculated activity coefficient value is then used in a simplified form of the solid-liquid equilibrium (SLE; solubility) equation (S1) to compute the DES curve and eutectic point:[1,2]

$$x_S^L = \frac{\exp\left(\frac{-\Delta H_{fus,S}}{RT_m}\left(\frac{1}{T}-\frac{1}{T_m}\right)\right)}{\gamma_S^L} \quad \text{(S1)}$$

Where $\Delta H_{fus,S}$ and T_m is the enthalpy of fusion and melting temperature of pure solute, respectively, R is the real gas constant, T is the absolute temperature, γ_S^L is the activity coefficient of a solute in the liquid phase, and x_S^L is the mole fraction (solubility) of solute in the liquid phase. The pure component fusion properties of investigated molecules were taken from the literature and reported in Table S4. The DES curve is calculated as the mutual solubility of HBA in HBD and HBD in HBA as a function of temperature and concentration. Figure S4 shows the COSMO-RS predicted eutectic point composition of both mDESs studied. From Figure S4, it was clear that the predicted eutectic point compositions ($ZnCl_2$:EG (1:4) and $ZnCl_2$:Gly (1:3)) are in great agreement with the experimental observations, demonstrating the robustness of the COSMO-RS model for calculating the eutectic points of mDESs.[3]

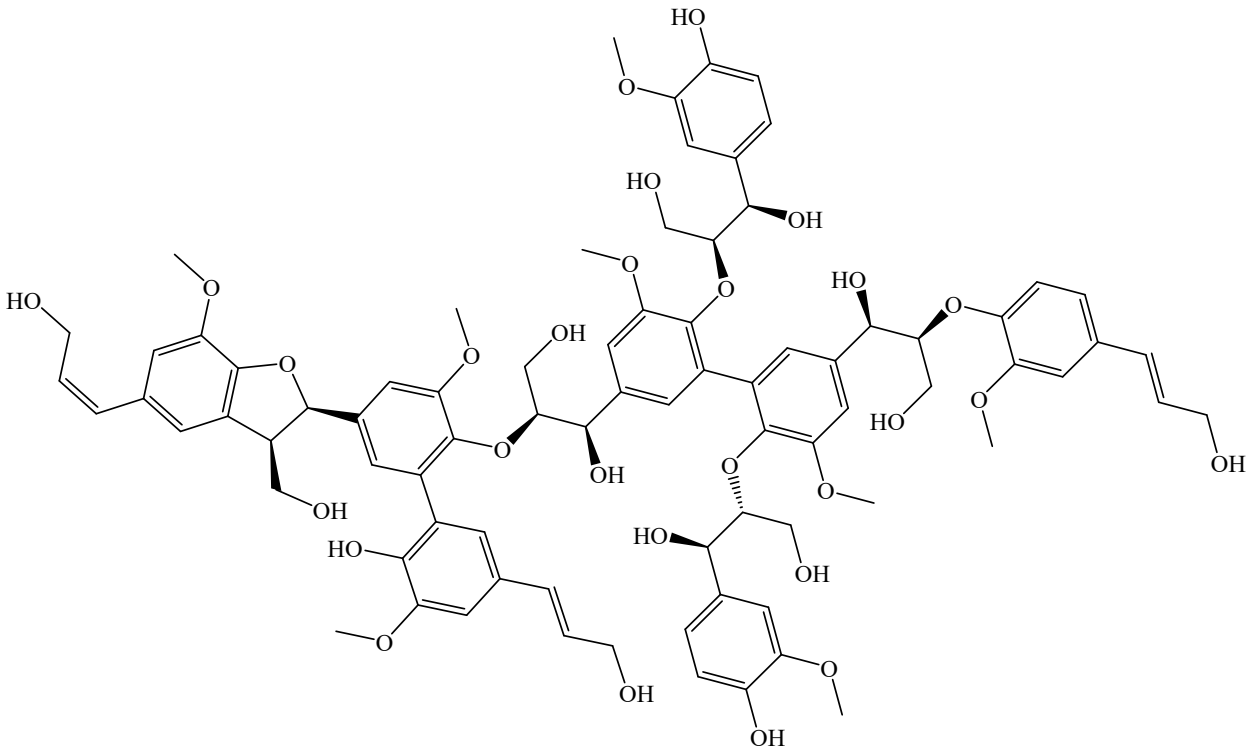


Figure S1: Chemical structures of lignin (DP = 8). The lignin molecule composed of all possible linkages such as β–5, 5–5, and β–O–4 linkages.

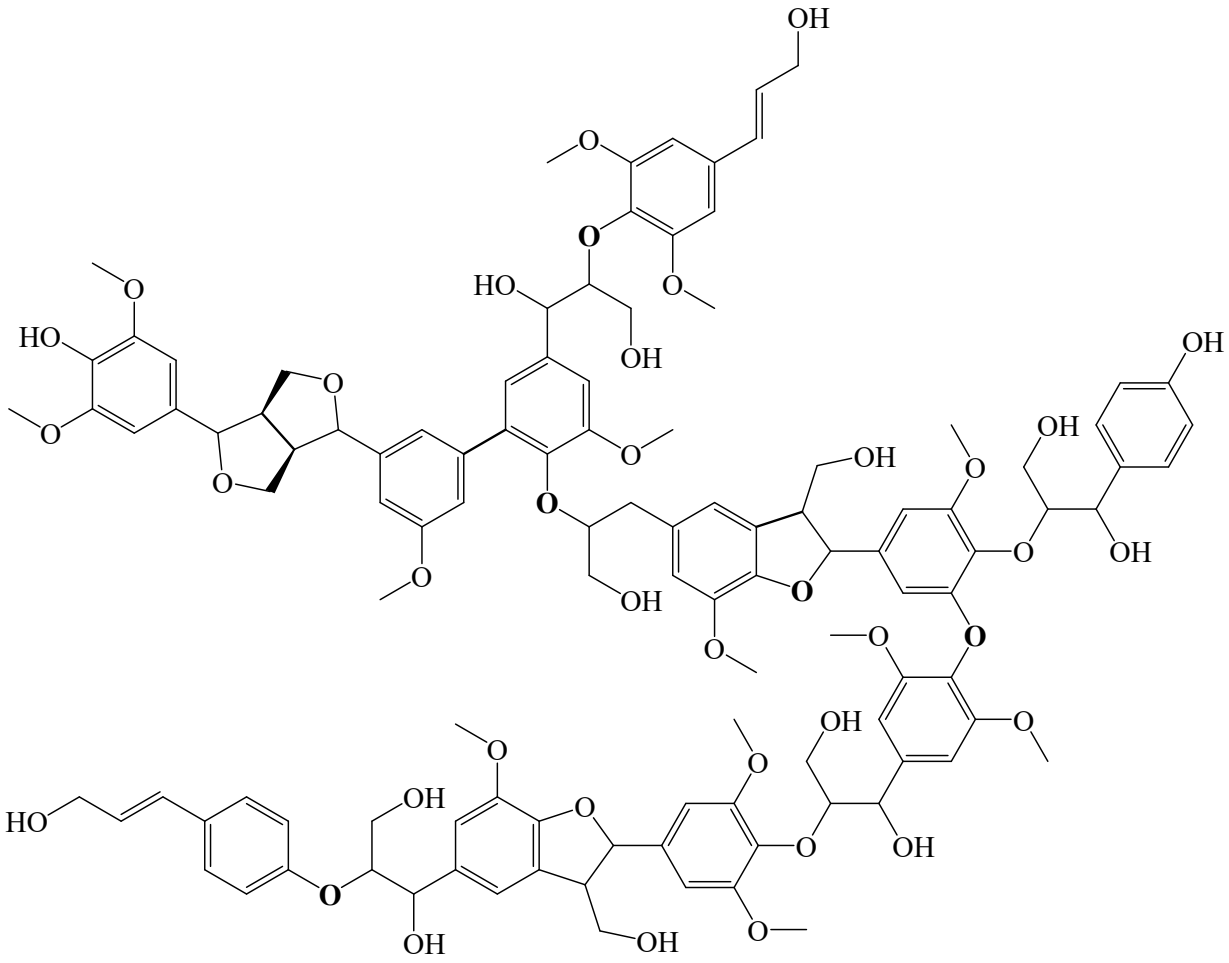


Figure S2: Chemical structures of lignin (DP = 11). The lignin molecule composed of all possible linkages such as β–β, β–5, 5–5, β–O–4, and 4–O–5 linkages.

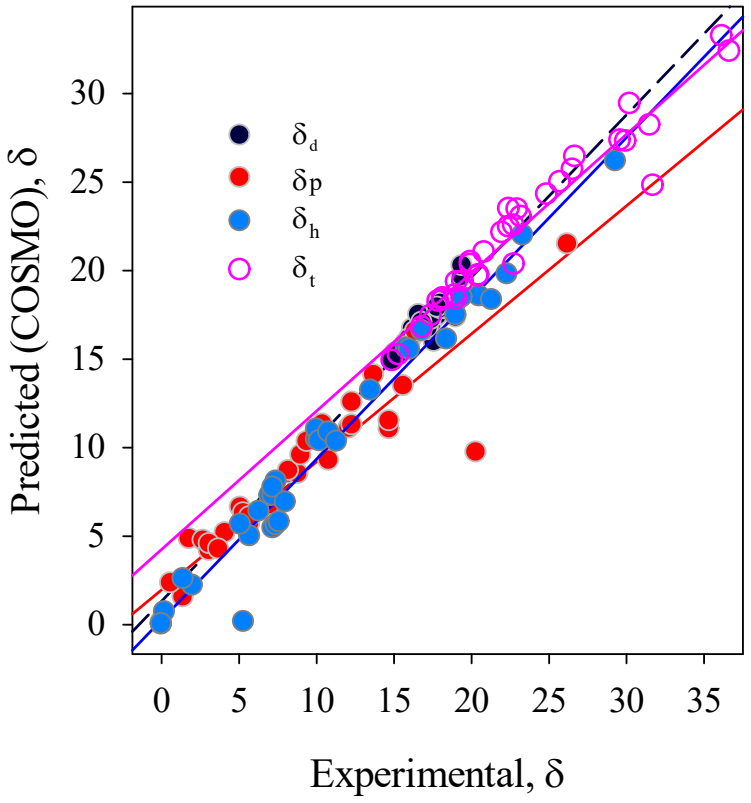


Figure S3: Predicted and experimental Hansen Solubility Parameters for Organic Solvents

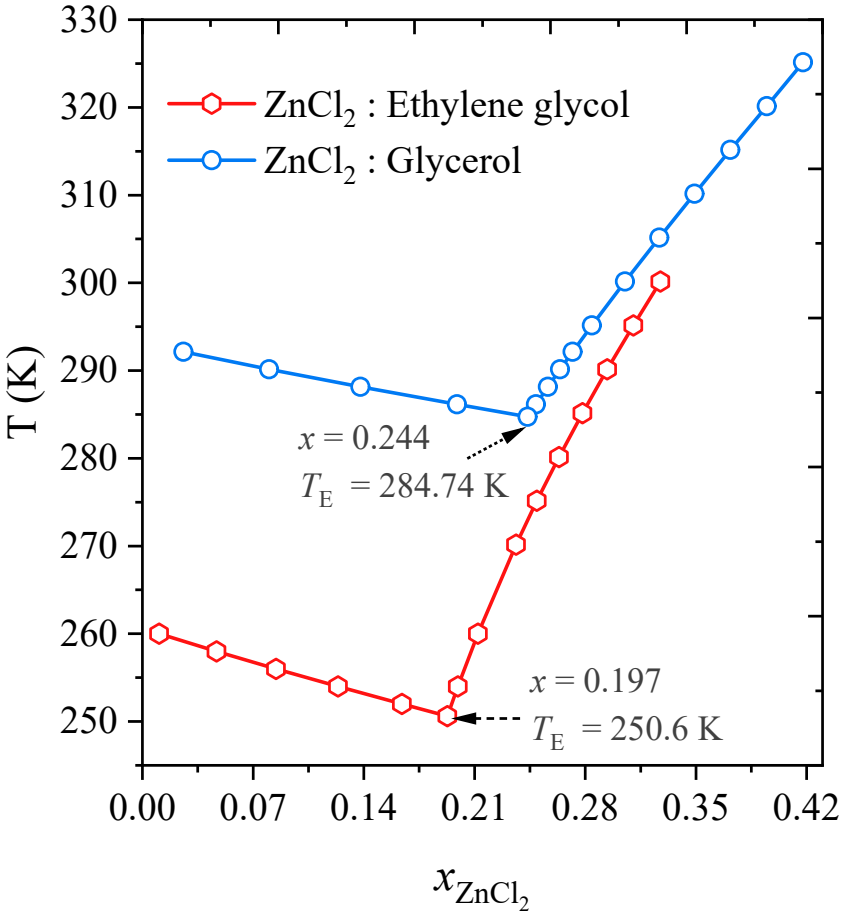


Figure S4: COSMO-RS predicted eutectic point composition of mDESs composed of zinc chloride with ethylene glycol and glycerol

Table S1: Densities (ρ) of Ionic liquids and deep eutectic solvents obtained from MD Simulations and compared with experimental density.

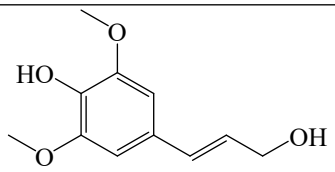
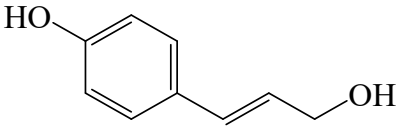
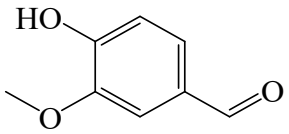
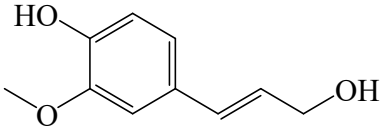
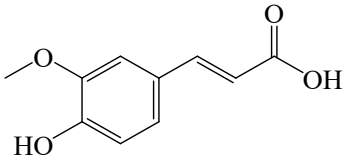
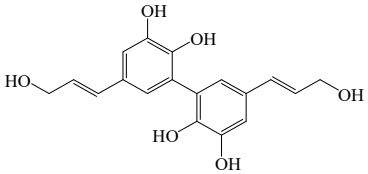
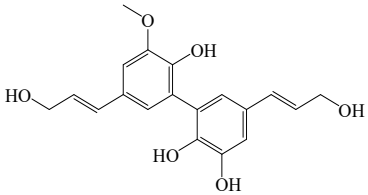
Ionic Liquid	ρ_{exp} (g/cc)	ρ_{MD} (g/cc)	Error (%)
[Ch][For]	-	1.138	-
[Ch][Ace]	1.10	1.081	1.73
[Ch][But]	1.07	1.043	2.52
[Ch][Hex]	1.02	0.997	2.25
[Ch][Oct]	-	0.970	-
[Ch][Lys]	1.09	1.062	2.57
[Ch][Lac]	1.14	1.130	0.88
[Emim][Ace]	1.10	1.112	1.09
[Emim][Lys]	-	1.071	-
$ZnCl_2$-EG (1:4)	-	1.342	-
$ZnCl_2$-Gly (1:3)	1.43	1.458	1.96

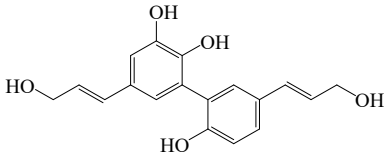
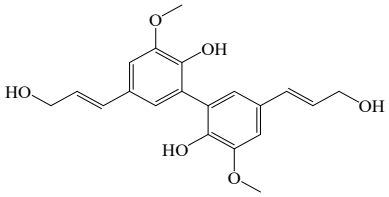
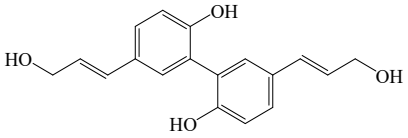
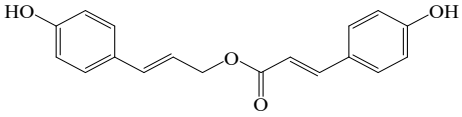
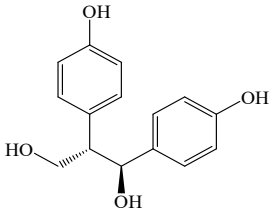
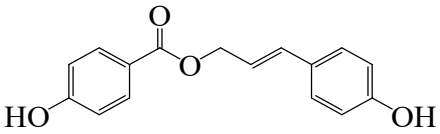
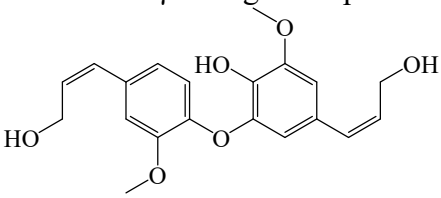
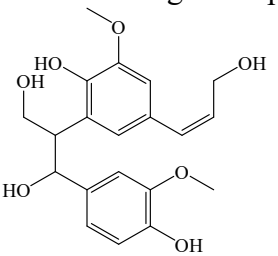
Table S2: Predicted Hansen Solubility Parameters Ionic Liquids and compared with the experimental values

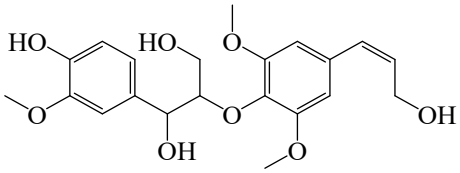
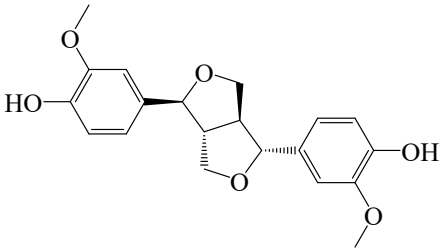
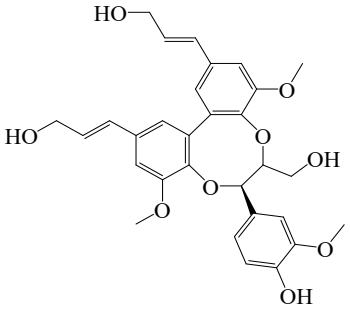
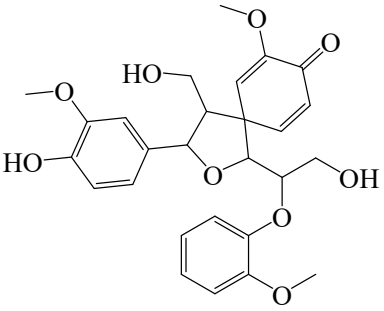
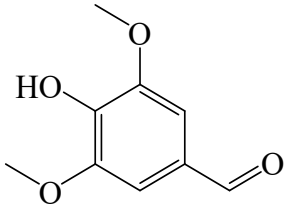
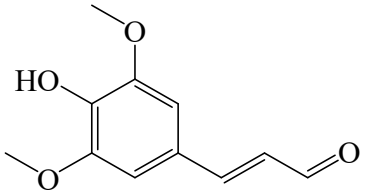
Ionic Liquid	COSMO-RS Predicted HSP ($MPa^{1/2}$)				Experimental[a,b]	Error (%)
	δ_d	δ_p	δ_h	δ_t		
[12OHEMIM][TF_2N]	18.43	11.61	13.37	25.56	26.49	3.51
[BMIM][HSO4]	18.10	11.21	12.79	24.84	23.10	7.52
[BMIM][PF_6]	18.60	11.33	9.34	23.70	23.20	2.16
[BMIM][TF_2N]	18.41	13.41	14.56	27.03	26.70	1.24
[EMIM][BF_4]	18.61	12.74	12.05	25.57	24.40	4.80
[EMIM][$EtSO_4$]	17.78	11.00	13.83	25.02	24.00	4.45
[BMIM][SCN]	18.09	10.80	12.65	24.58	24.64	0.25
[BMIM][$MeSO_4$]	18.20	11.12	12.57	24.76	23.3	6.25
[BMPyr][DCN]	18.47	12.83	12.03	25.52	25.54	0.08

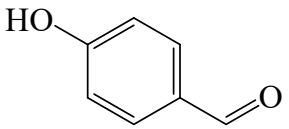
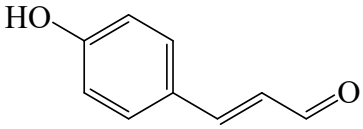
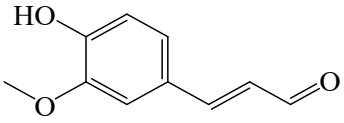
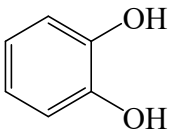
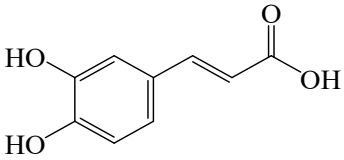
[a] Data taken from Weerachanchai *et al.* (2012)[4]; [b] Yoo *et al.* (2012)[5]

Table S3: COSMO-RS-based predicted Hansen solubility parameters of lignin monomers, dimers and trimers

Lignin structure	COSMO-RS predicted HSP ($MPa^{1/2}$)			
	δ_d	δ_p	δ_h	δ_t
 Sinapyl alcohol	18.45 19.2[a]	10.92 7.3[a]	14.56 16.1[a]	25.92 26.1[a]
 p-Coumaryl alcohol	18.41 19.2[a]	11.38 7[a]	14.40 17.3[a]	26.0 26.7[a]
 Vanillin	18.58 19.6[a]	12.83 10.7[a]	13.81 12.5[a]	26.47 25.6[a]
 Coniferyl alcohol	18.41 19[a]	12.15 7[a]	14.43 16.3[a]	26.36 26[a]
 Ferulic acid	18.41 19.8[a]	13.09 7.6[a]	14.95 15.8[a]	27.08 26.4[a]
 CAT 5–5 CAT	18.39	12.63	23.35	32.29
 CAT 5–5 GUAI	18.38	12.45	21.90	31.18

 CAT 5–5 PHP	18.39	12.77	22.73	31.91
 GUAI 5–5 GUAI	18.38	11.32	21.51	30.47
 PHP 5–5 PHP	18.38	12.05	22.08	31.15
 PHP γ–O–γ linkage Compound	18.38	10.89	20.78	29.80
 PHP β–1 linkage Compound	18.38	12.04	21.80	30.95
 PHP α–O–γ linkage Compound	18.37	11.23	20.64	29.83
 GUAI 4–O–5 linkage Compound	18.37	10.14	19.03	28.33
 Lignin β–5 linkage Compound	18.38	12.25	22.14	31.28

 Lignin β–O–4 linkage Compound	18.38	10.67	19.70	28.97
 Lignin β–β linkage Compound	18.37	9.93	21.04	29.64
 Dibenzodioxocin	18.36	9.29	17.86	27.41
 Spirodienone	18.39	10.15	19.23	28.48
 Syringaldehyde	18.46	12.80	14.60	26.79
 Sinapylaldehyde	18.45	12.78	14.82	26.90

 p-Hydroxy benzaldehyde	18.42	13.71	16.78	28.44
 p-Coumaraldehyde	18.40	12.99	20.69	30.58
 Coniferaldehyde	18.46	12.81	13.97	26.46
 Catechol	18.35	12.63	22.79	31.86
 Caffeic acid	18.33	13.17	21.55	31.20

[a] Data taken from Hansen (2007)[6]

Table S4: Melting point and heat of fusion of HBA and HBD of mDESs investigated in this work

Name of the compound	T_m (K)	ΔH_f	Reference
$ZnCl_2$	581.25	3.886	Trivedi et al. (2017)[7]
Ethylene glycol	260.60	9.958	Nikolaev and Rabinovich, 1967[8]
Glycerol	293.15	18.285	Acree, 1991[9]

References

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