Electronic Supplementary Material (ESI) for Green Chemistry.

Molecular simulations inform biomass dissolution in ionic liquids in pursuit of benign solvent-system design

Preston Griffin[a] and Jakub Kostal*[a]

Table S1: A complete list of ILs, corresponding solubility metrics obtained from experiment and computed values for biomass dissolution and ecotoxicity as used in the present analysis [a]

IL	Lignin solubility (g/kg)	T (°C)	Exptl study[1-4]	Pred. sol. Coulomb/LJ (g/kg)	Log $P_{L/C}$ (exptl source)	Log $P_{o/w}$	ΔE, HOMO-LUMO gap (eV)
[Bm2im][BF4]	14.50	120.0	Pu et al.	54.8/26.6	-0.16 (L)	2.98	6.74
[Bmim][Br]	17.50	75.00	Pu et al.	60.4/65.3	-1.10 (LC)	5.32	7.25
[Bmim][Cl]	13.90	75.00	Pu et al.	28.2/83.4	1.26(LC)	6.26	6.18
[Bmim][$MeSO_4$]	61.80	25.00	Pu et al.	135.7/49.7	-0.22(LC)	6.08	6.10
[Bmim][$MeSO_4$]	312.00	50.00	Pu et al.	378.3/244.8	0.49(LC)	6.98	6.10
[Bmim][PF_6]	0	120.0	Pu et al.	23.3/64.0	N/A(LC)	5.56	8.00
[Bmpy][PF_6]	0	120.0	Pu et al.	9.4/53.5	N/A(LC)	7.88	5.99
[Hmim][CF_3SO_3]	10.00	50.00	Pu et al.	23.9/172.8	-1.41(LC)	2.89	10.47
[Hmim][CF_3SO_3]	275.00	70.00	Pu et al.	224.2/111.1	0.03(LC)	2.89	10.47
[Mmim][$MeSO_4$]	74.20	25.00	Pu et al.	72.4/200	0.29(LC)	2.13	5.21
[Mmim][$MeSO_4$]	344.00	50.00	Pu et al.	284.4/40.9	0.77(LC)	2.13	5.21
[Py][For]	280.00	25.00	Pu et al.	205.6/152.4	1.02(L)	1.42	1.66
[Ch][Ala]	180.00	90.00	Liu et al.	263.4/143.3	1.56(LC)	-2.94	6.73
[Ch][Arg]	110.00	90.00	Liu et al.	112.0/119.0	1.34(LC)	-4.03	6.76
[Ch][Asn]	16.00	90.00	Liu et al.	295.3/147.6	0.51(LC)	-3.27	6.47
[Ch][Asp]	10.00	90.00	Liu et al.	244.9/74.4	0.30(LC)	-1.44	7.79
[Ch][Gln]	50.00	90.00	Liu et al.	106.2/273.1	1.00(LC)	-2.93	6.97
[Ch][Glu]	26.00	90.00	Liu et al.	189.8/54.5	0.72(LC)	-1.26	4.43
[Ch][Gly]	220.00	90.00	Liu et al.	172.1/299.1	1.64(LC)	-2.88	7.23
[Ch][His]	140.00	90.00	Liu et al.	170.2/201.1	1.45(LC)	-2.71	7.27
[Ch][Ile]	170.00	90.00	Liu et al.	24.9/8.8	1.53(LC)	-1.87	6.71
[Ch][Leu]	150.00	90.00	Liu et al.	240/64.4	1.48(LC)	-2.09	6.37
[Ch][Lys]	140.00	90.00	Liu et al.	258.8/60.4	1.45(LC)	-3.34	4.42
[Ch][Met]	150.00	90.00	Liu et al.	19.29/132.3	1.47(LC)	-2.02	6.86
[Ch][Phe]	140.00	90.00	Liu et al.	200.0/15.0	1.45(LC)	-1.70	5.56
[Ch][Pro]	170.00	90.00	Liu et al.	162.2/52.0	1.53(LC)	-1.11	5.35

[Ch][Ser]	170.00	90.00	Liu et al.	179.3/20.8	1.53(LC)	-1.96	6.93
[Ch][Thr]	160.00	90.00	Liu et al.	147.0/176.9	1.51(LC)	-3.31	4.99
[Ch][Trp]	90.00	90.00	Liu et al.	42.8/115.8	1.26(LC)	-0.98	6.63
[Ch][Val]	70.00	90.00	Liu et al.	63.8/43.6	1.15(LC)	-2.18	7.35
[BMPyr][Tf_2N]	1.00	90.00	Glas et al.	38.4/18.6	2.77(L)	5.17	7.25
[BMPyr][$N(CN)_2$]	390.00	90.00	Glas et al.	165.0/306.3	3.36(L)	2.98	6.98
[Ch][Oac]	280.00	90.00	Glas et al.	148.5/266.9	2.71(L)	-1.12	6.95
[p4441][Cl]	330.00	90.00	Glas et al.	160.7/191.2	0.72(L)	0.15	4.66
[p4441][$MeSO_4$]	460.00	90.00	Glas et al.	221.7/126.8	0.58(L)	1.43	8.12
[p66614][$N(CN)_2$]	270.00	90.00	Glas et al.	113.6/83.4	0.22(L)	11.72	3.93
[Mmim][Ac]	500.00	90.00	Rashid et al.	96.8/81.0	0.40(L)	-0.69	7.07
[Py][Ac]	240.00	25.00	Rashid et al.	151.9/36.5	0.95(L)	-2.46	1.83
[Py][Ac]	700.00	75.00	Rashid et al.	205.8/10.2	1.42(L)	-2.46	1.83
[Py][Pro]	500.00	90.00	Rashid et al.	11.5/15.6	1.57(L)	-0.40	3.48
[Pyrr][Ac]	500.00	90.00	Rashid et al.	16.0/117.4	0.68(L)	-1.35	7.36

[a] Bm2im = 1-butyl-2,3-dimethylimidazolium; Bmim = 1-butyl-3-methylimidazolium; Bmpy = 1-butyl-3-methylpyridinium; Hmim = 1-hexyl-3-methylimidazolium; Mmim = 1,3-dimethylimidazolium; Py = pyridinium; BMPyr = 1-butyl-1-methylpyrrolidinium; Chol = cholinium; p4441 = tributyl methyl phosphonium; p66614 = trihexyl-tetradecylphosphonium; Pyrr = pyrrolidinium;

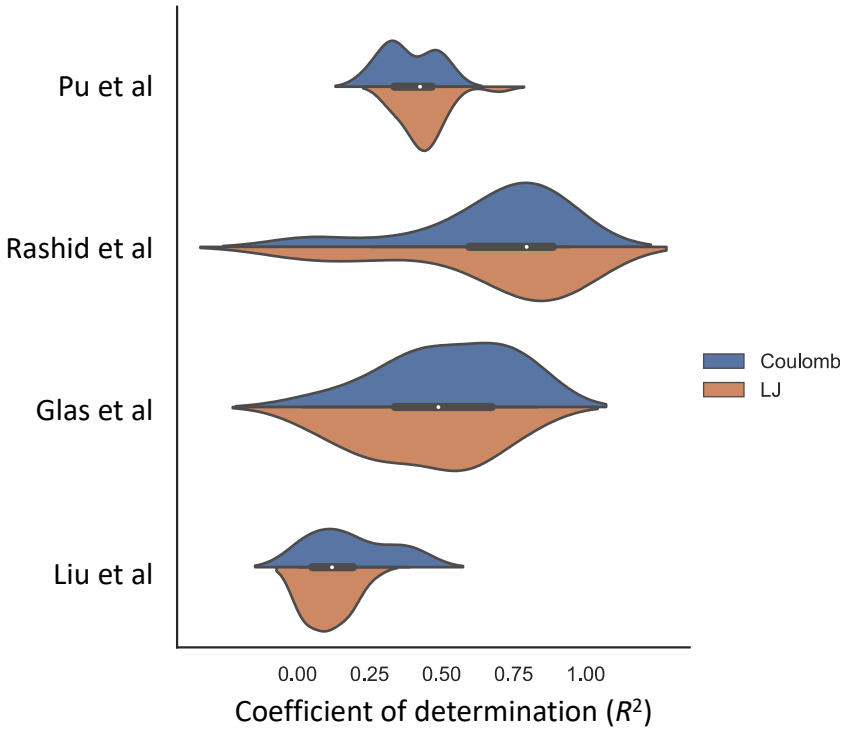


Figure S1. Distributions of coefficients of determination (R^2) for univariate models correlating interaction energies (Coulomb or Lennard-Jones, LJ) and observed solubility, compiled per study across the 4 computational adaptations of guaiacyl glycerol-β-guaiacyl ether (GG) in Kraft lignin (viz. Figure 2). The white dot inside each violin plot represents the median R2 value, and the grey bar represents the interquartile range (i.e., middle 50%).

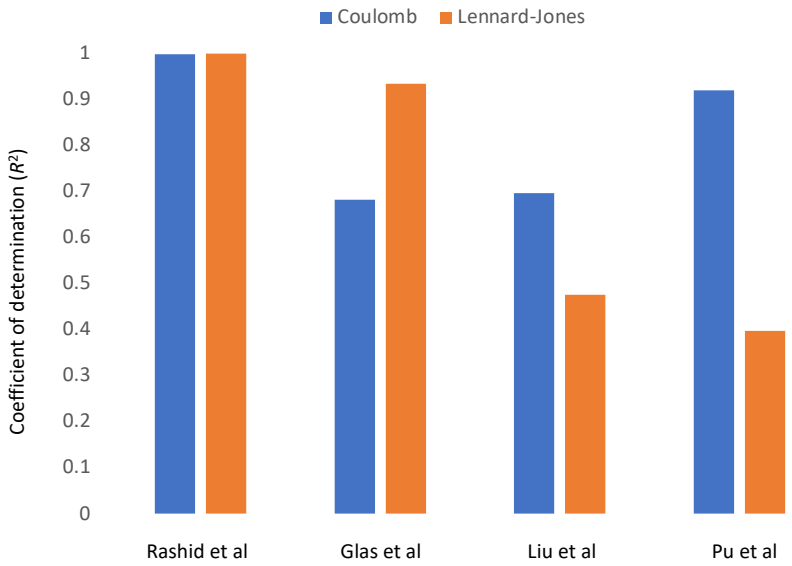
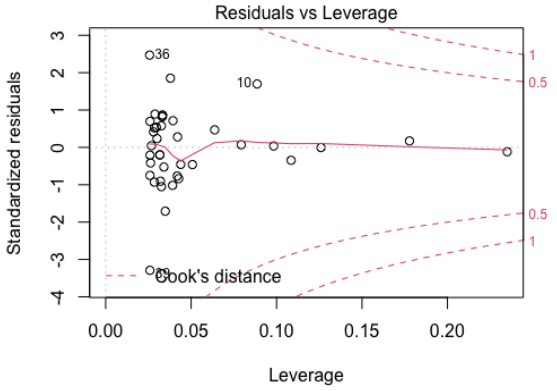


Figure S2. Coefficients of determination (R^2) for multivariate linear regressions (MLRs), developed for each study by correlating interaction energies (Coulomb or Lennard-Jones, LJ) with observed solubility across the 4 computational adaptations of guaiacyl glycerol-β-guaiacyl ether (GG) in Kraft lignin (viz. Figure 2).

a)



b)

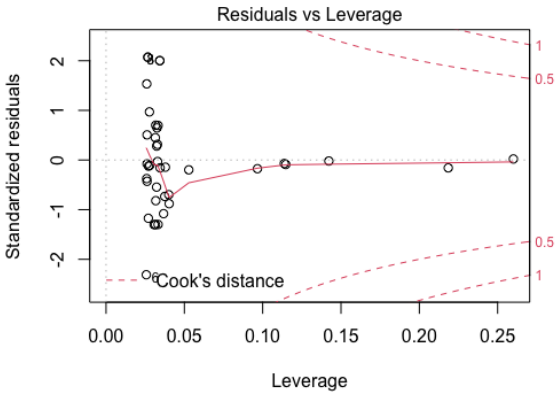


Figure S3. Williams plot used to evaluate the applicability domain (AD) of (a) Coulomb model and (b) LJ model.

Reference:

1. Pu, Y.; Jiang, N.; Ragauskas, A. J. Ionic Liquid as a Green Solvent for Lignin. Journal of Wood Chemistry and Technology 2007, 27 (1). https://doi.org/10.1080/02773810701282330.
2. Liu, Q.-P.; Hou, X.-D.; Li, N.; Zong, M.-H. Ionic Liquids from Renewable Biomaterials: Synthe-sis, Characterization and Application in the Pretreatment of Biomass. Green Chem. 2012, 14 (2). https://doi.org/10.1039/C2GC16128A.
3. Glas, D.; van Doorslaer, C.; Depuydt, D.; Liebner, F.; Rosenau, T.; Binnemans, K.; de Vos, D. E. Lignin Solubility in Non-Imidazolium Ionic Liquids. Journal of Chemical Technology & Biotech-nology 2015, 90 (10). https://doi.org/10.1002/jctb.4492.
4. Rashid, T.; Kait, C. F.; Regupathi, I.; Murugesan, T. Dissolution of Kraft Lignin Using Protic Ion-ic Liquids and Characterization. Ind Crops Prod 2016, 84. https://doi.org/10.1016/j.indcrop.2016.02.017.