Supporting Information for "Improved Prediction of Phase Behaviors of Ionic Liquid Solutions with Consideration of Directional Hydrogen Bonding Interactions"

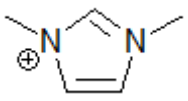
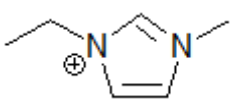
Chun-Kai Chang and Shiang-Tai Lin*

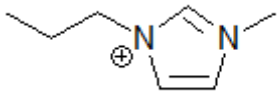
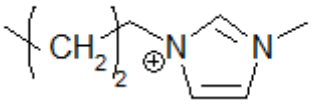
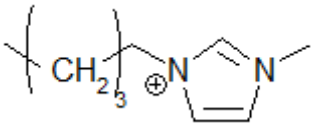
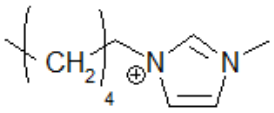
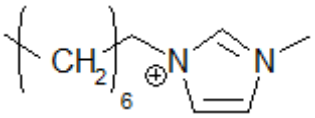
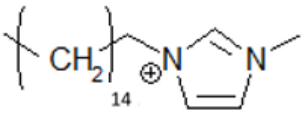
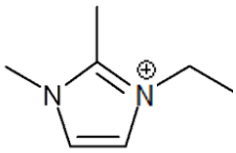
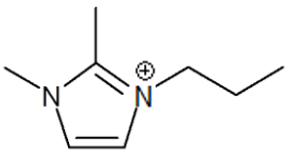
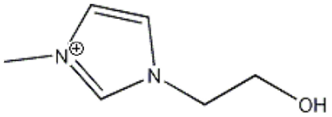
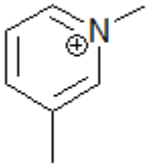
Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

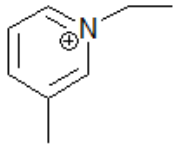
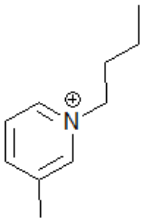
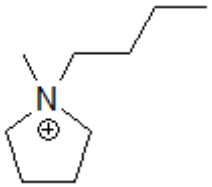
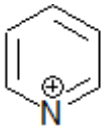
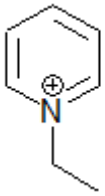
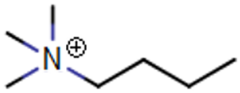
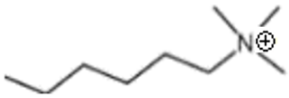
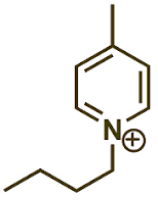
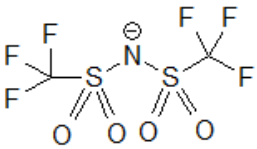
S1. Cations and Anions of IL Examined in This Work

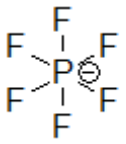
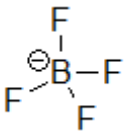
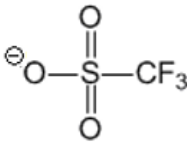
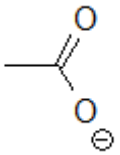
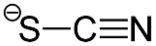
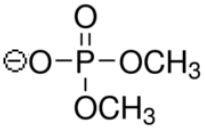
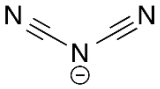
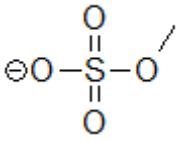
In this section, we provide the cations and anions of ILs examined in this work. In general, most of cations are imidazolium-based ion (e.g. [C_xMIM], x = 1, 2, 3...) and most of anions have HB acceptor atoms connected to the third row atoms in the period table (e.g. S and P) such as [$MeSO_4$] and [DC_1Ph] or F-contained molecules. It is worth to mention that the lone pairs of these anions cannot be determined from the previous VSEPR method.[1] The cations and anions of IL examined in this work are listed in Table S1. For compounds that demonstrated in the main text, the corresponding hbc, COSMO surface, HB surface determined by COSMO-SAC 2018, and HB-level σ-profile are provided in Table S2. For those compounds that have multiple local minima

Table S1. Summary of cations and anions of ionic liquids considered in this work

Cation /Anion	Formula	Name	Chemical Structure
[C_1MIM]	$C_5H_9N_2$	1,3-dimethylimidazolium	
[C_2MIM]	$C_6H_{11}N_2$	1-ethyl-3-methylimidazolium	

[C_3MIM]	$C_7H_{13}N_2$	1-propyl-3-methylimidazolium	
[C_4MIM]	$C_8H_{15}N_2$	1-butyl-3-methylimidazolium	
[C_5MIM]	$C_9H_{17}N_2$	1-pentyl-3-methylimidazolium	
[C_6MIM]	$C_{10}H_{19}N_2$	1-hexyl-3-methylimidazolium	
[C_8MIM]	$C_{12}H_{23}N_2$	1-octyl-3-methylimidazolium	
[C_{16}MIM]	$C_{20}H_{39}N_2$	1-hexadecyl-3-methylimidazolium	
[C_2DMIM]	$C_7H_{13}N_2$	1-ethyl-2,3-dimethylimidazolium	
[C_3DMIM]	$C_8H_{15}N_2$	1,2-dimethyl-3-propylimidazolium	
[EOHMIM]	$C_6H_{11}N_2O$	1-(2-hydroxyethyl)-3-methylimidazolium	
[C_1Mpy]	$C_7H_{10}N$	1,3-dimethylpyridinium	

[C_2Mpy]	$C_8H_{12}N$	1-ethyl-3-methylpyridinium	
[C_4Mpy]	$C_{10}H_{16}N$	1-butyl-3-methylpyridinium	
[C_4Mpyrr]	$C_9H_{20}N$	1-butyl-1-methylpyrrolidinium	
[py]	C_5H_6N	Pyridinium	
[C_2py]	$C_7H_{10}N$	1-ethylpyridinium	
[C_4TMA]	$C_7H_{18}N$	N-butyl-N,N,N-trimethylammonium	
[C_6TMA]	$C_9H_{22}N$	N,N,N-trimethyl-1-hexanaminium	
[C_4C_1py]	$C_{10}H_{16}N$	N-butyl-4-methylpyridinium	
[TF_2N]	$C_2F_6NO_4S_2$	bis-(trifluoromethylsulfonyl)	

		imide	
[PF_6]	F_6P	hexafluorophosphate	
[BF_4]	BF_4	tetrafluoroborate	
[OTF]	CF_3O_3S	trifluoromethylsulfonate	
[Ac]	$C_2H_3O_2$	Acetate	
[Br]	Br	Bromide	Br^-
[I]	I	Iodide	I^-
[Cl]	Cl	Chloride	Cl^-
[CNS]	CNS	thiocyanate	
[DC_1Ph]	$C_2H_6O_4P$	dimethylphosphate	
[DCN]	C_2N_3	dicyanamide	
[$MeSO_4$]	CH_3O_4S	methylsulfate	

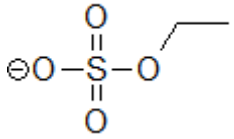
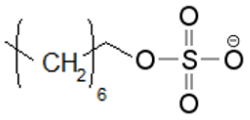
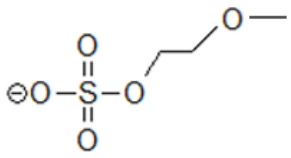
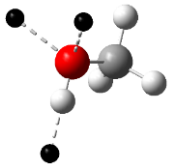
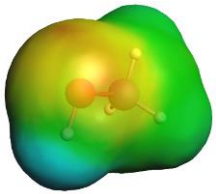
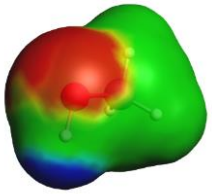
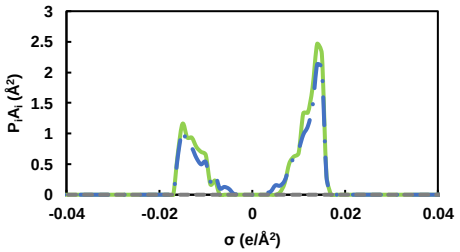
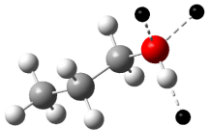
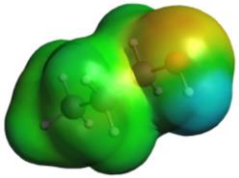
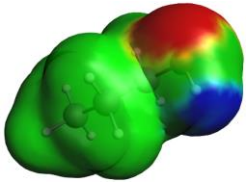
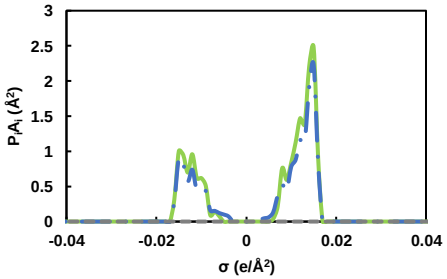
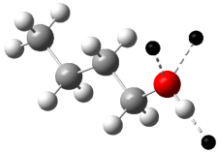
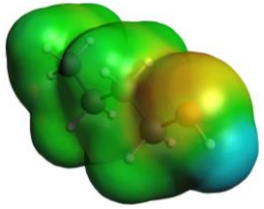
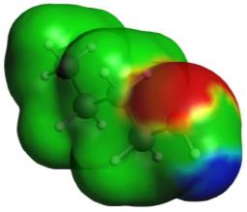
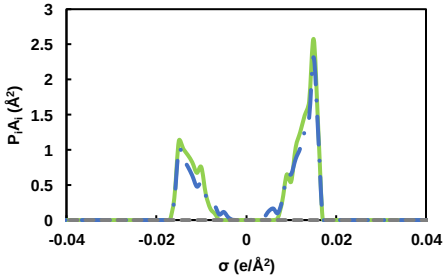
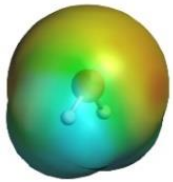
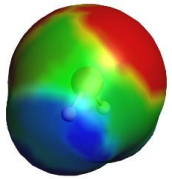
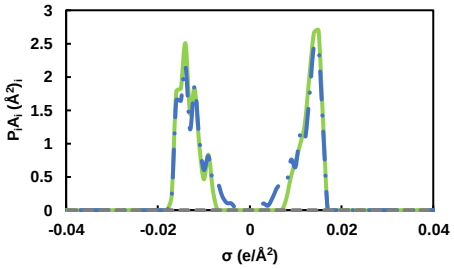
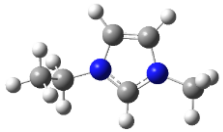
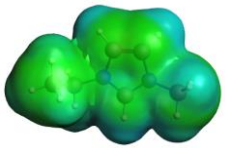
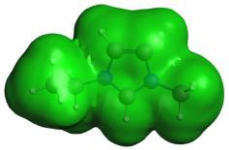
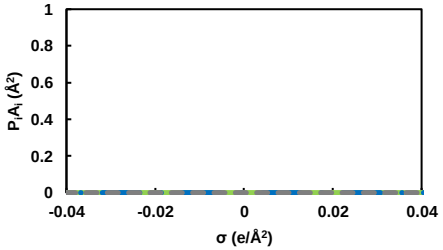
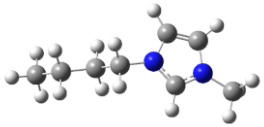
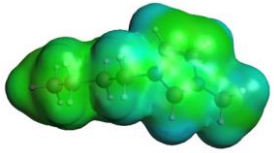
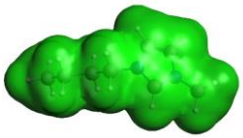
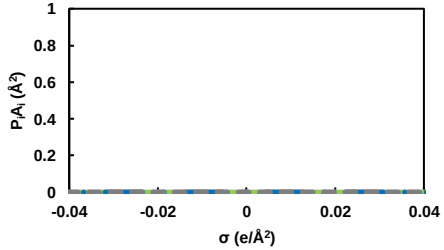
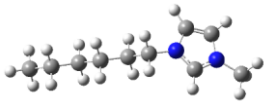
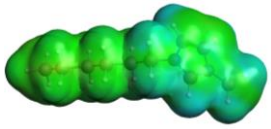
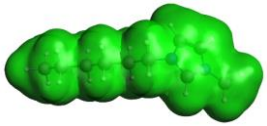
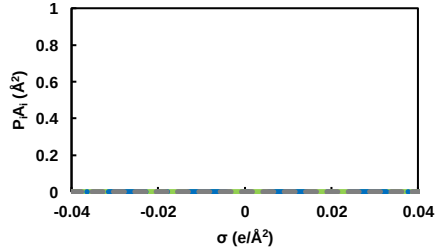
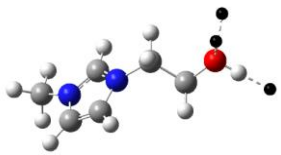
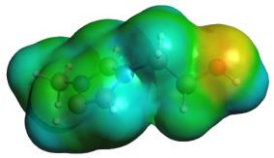
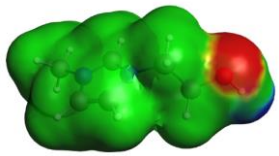
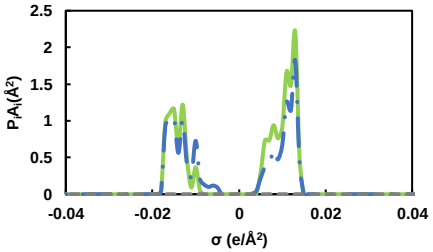
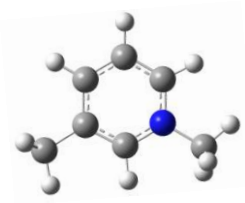
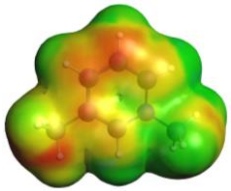
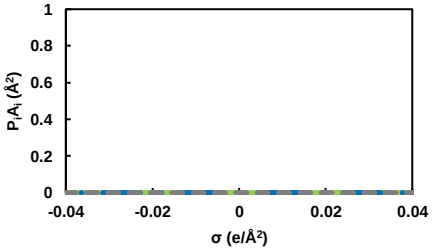
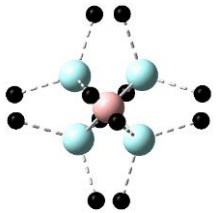
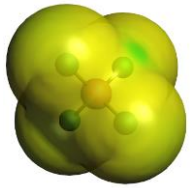
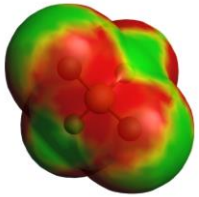
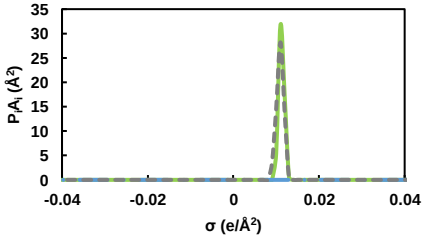
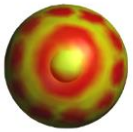
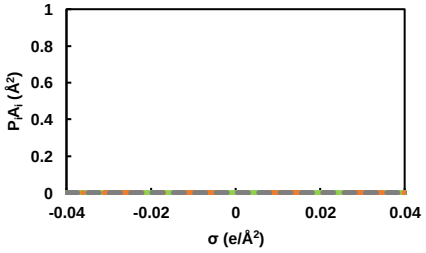
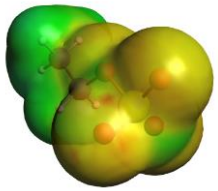
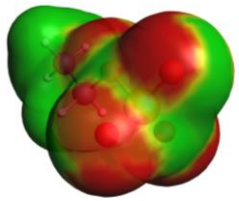
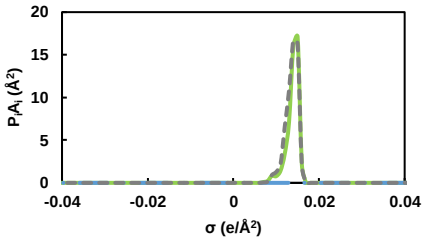
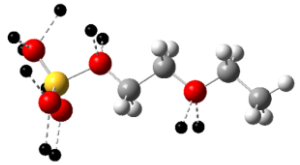
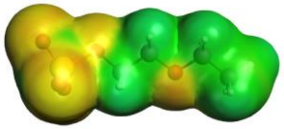
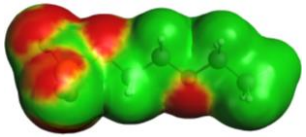
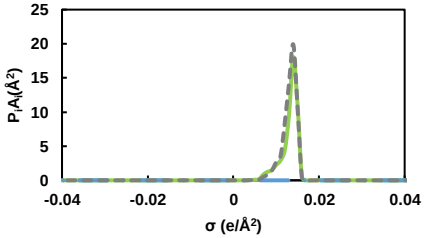
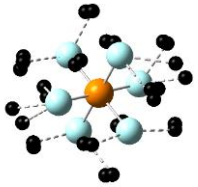
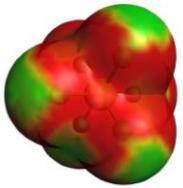
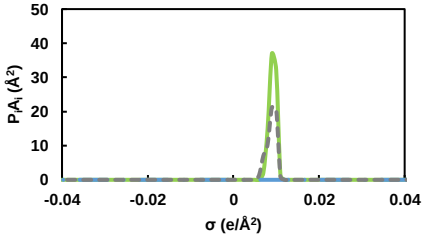
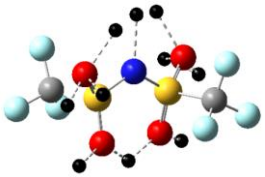
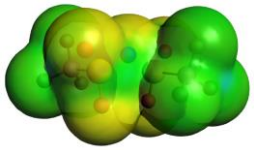
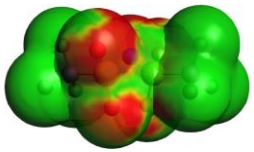
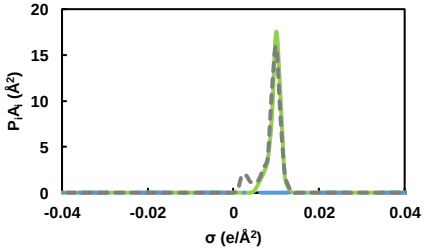
[$EtSO_4$]	$C_2H_5O_4S$	ethylsulfate	
[C_8SO_4]	$C_8H_{17}O_4S$	octylsulfate	
[$MOEtSO_4$]	$C_3H_7O_5S$	methoxyethylsulfate	

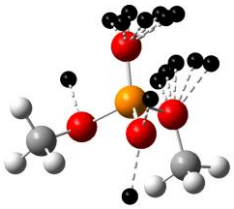
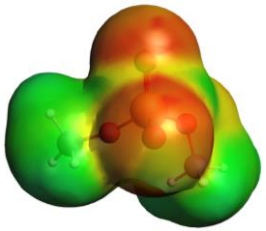
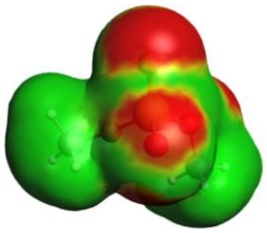
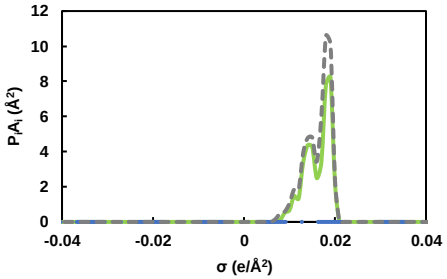
Table S2. Some examples of hbc, HB surfaces, and σ-profiles in HB-level of the molecules discussed in this work.

Name	Full Name	Geometry & hbc	COSMO surface -0.0025 0.0025 (e/Å²)	Directional HB surface donor acceptor	HB-level σ-profile 2010 (OH) 2010 (OT) 2018
Methanol	Methanol				
1-Propanol	1-Propanol				
1-Butanol	1-Butanol				

Water	Water				
[C_2MIM]	1-ethyl-3-methylimidazolium				
[C_4MIM]	1-n-butyl-3-methylimidazolium				
[C_6MIM]	1-hexyl-3-methylimidazolium				

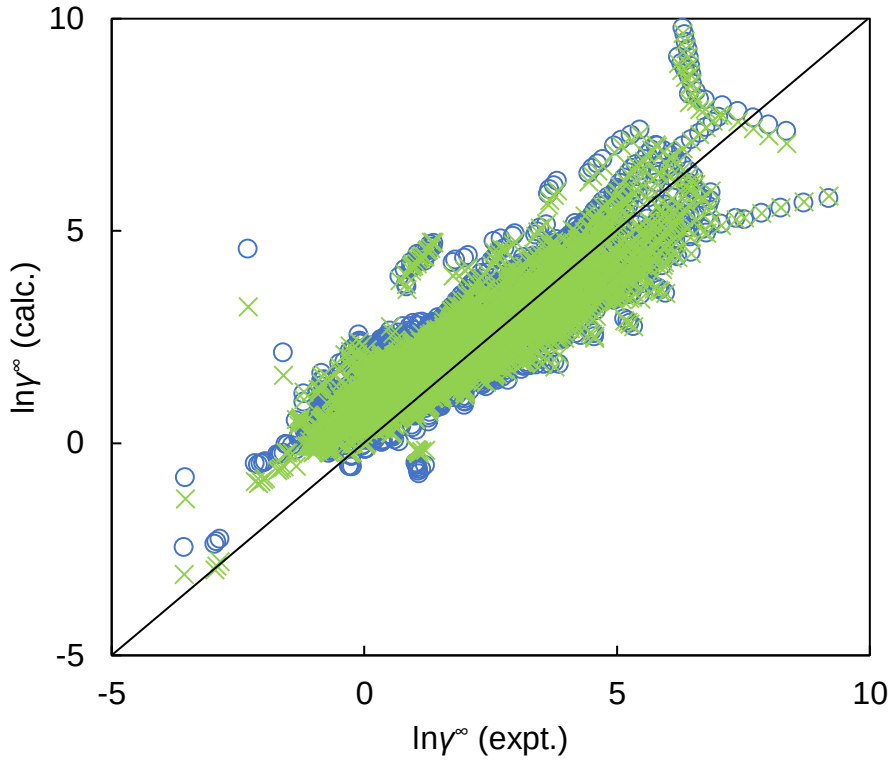
[EOHMIM]	1-(2-hydroxyethyl)-3-methylimidazolium				
[C_1MPy]	1,3-dimethylpyridinium				
[BF_4]	Tetrafluoroborate				
[Cl]	Chloride				

[$EtSO_4$]	Ethylsulfate				
[$EOEtSO_4$]	Ethoxyethylsulfate				
[PF_6]	Hexafluorophosphate				
[TF_2N]	Bis(trifluoromethylsulfonyl)imide				

[DC_1Ph]	Dimethylphosphate				

S2. Detail Results for IDAC, Osmotic Coefficient, LLE, and VLE Results of Demonstrated Examples

(a)



(b)

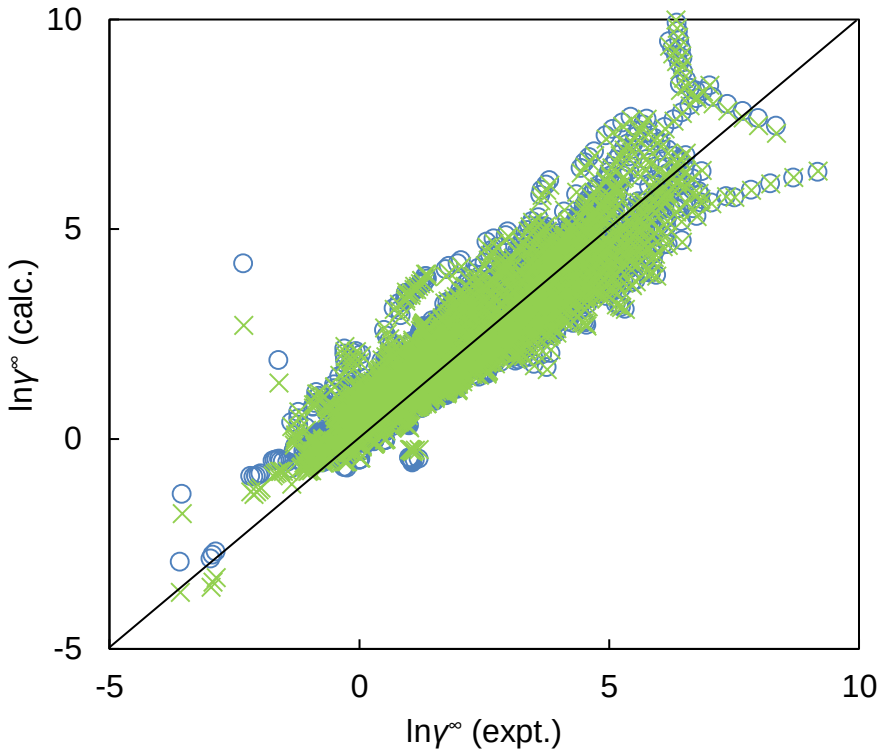
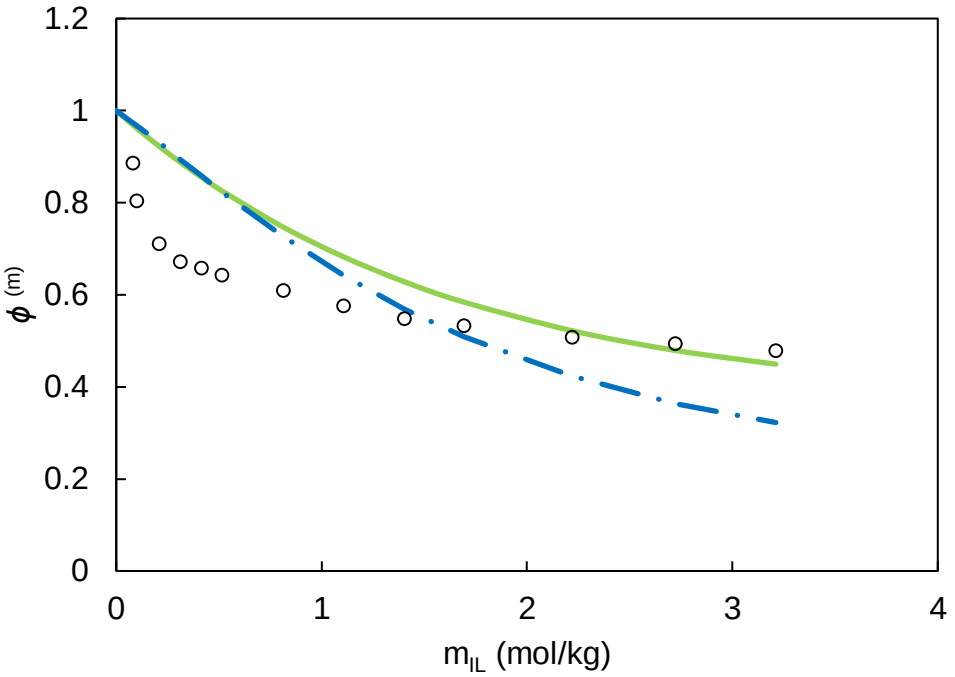
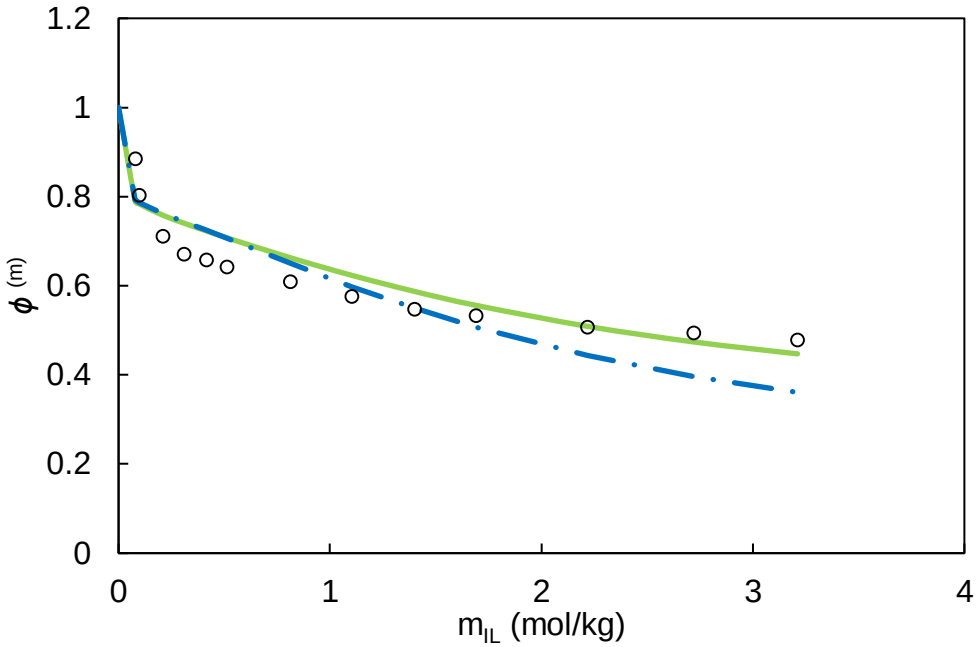


Fig. S1 The IDAC of neutral species in ILs predicted by COSMO-SAC models with (a) $\alpha = 1$ (b) $\alpha_0 = 0.35$. (COSMO-SAC 2010: blue circles ○ ; COSMO-SAC 2018: green crosses ×)

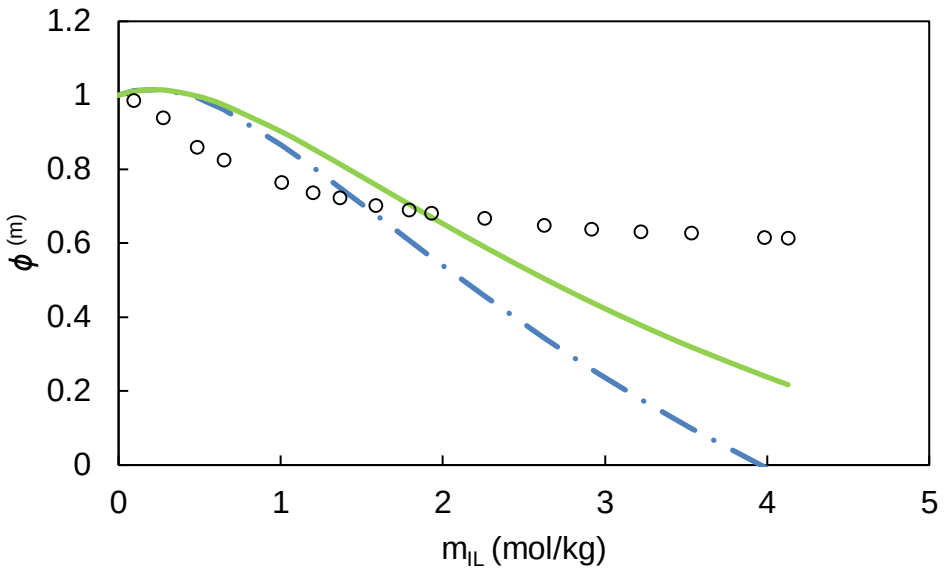
(a)


1.2
1
0.8
0.6
0.4
0.2
0
ϕ (m)
0
1
2
3
4
m_IL (mol/kg)

(b)


1.2
1
0.8
0.6
0.4
0.2
0
ϕ (m)
0
1
2
3
4
m_IL (mol/kg)

(c)



(d)

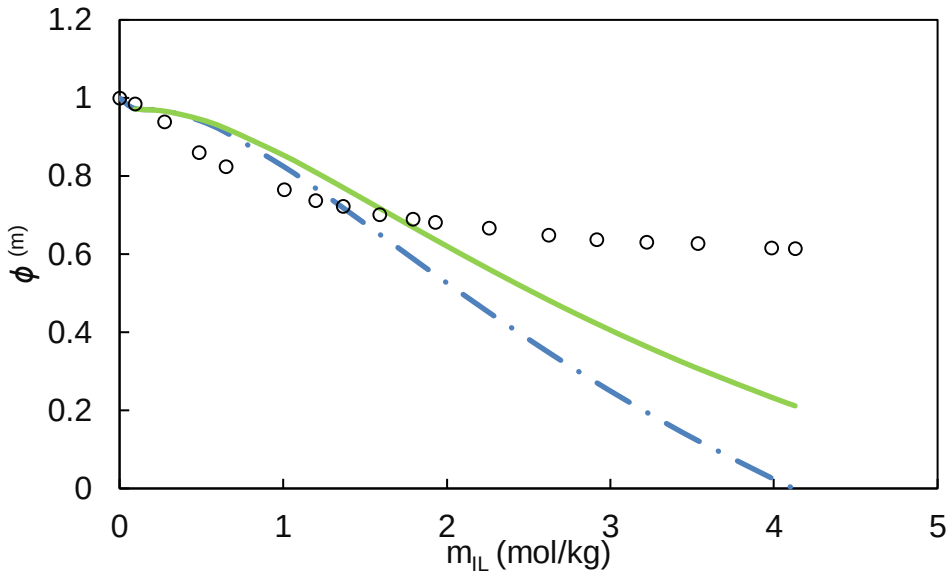
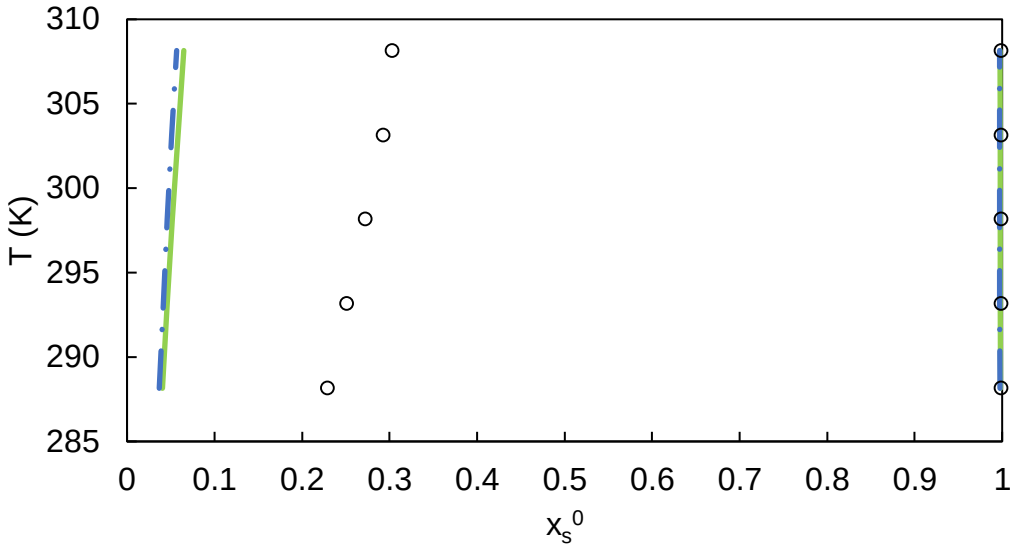
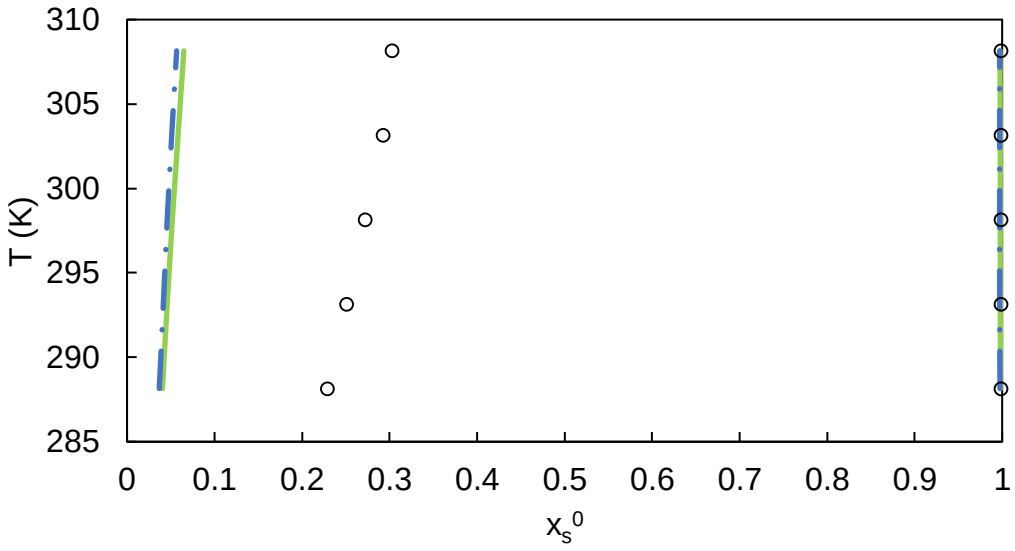


Fig. S2 The osmotic coefficient of 1-propanol-[C_1MPy][$MeSO_4$] at 323.15 K[2]: (a) $\alpha = 0$ (b) $\alpha_0 = 0.35$ and water-[C_6MIM][Cl] binary system at 313.15 K[3]: (c) $\alpha = 0$ (d) $\alpha_0 = 0.35$ predicted by COSMO-SAC models. (COSMO-SAC 2010: blue chain lines - · - · - ; COSMO-SAC 2018: green solid lines ——; experimental data: black circles ○)

(a)


310
305
300
295
290
285
T (K)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
x_s^0

(b)


310
305
300
295
290
285
T (K)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
x_s^0

(c)

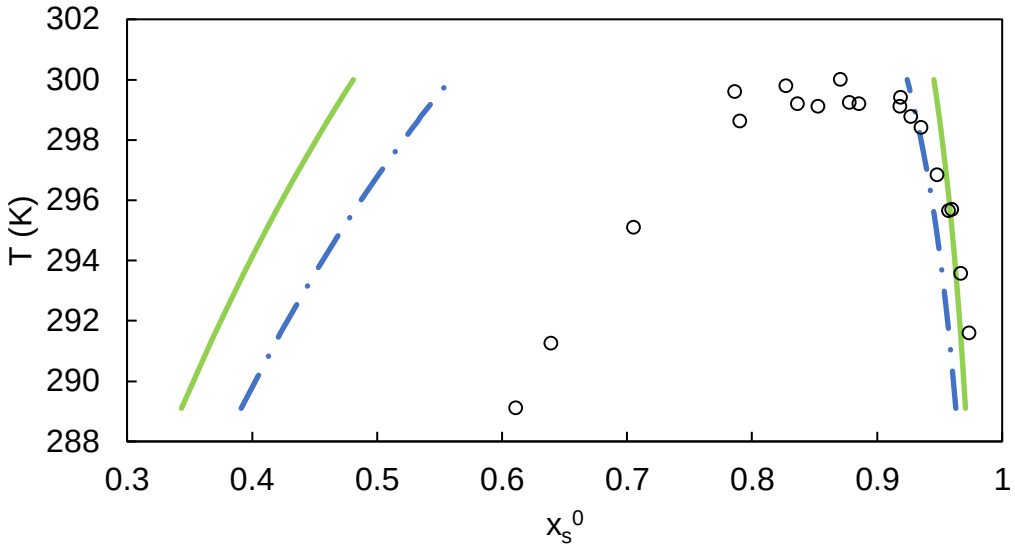
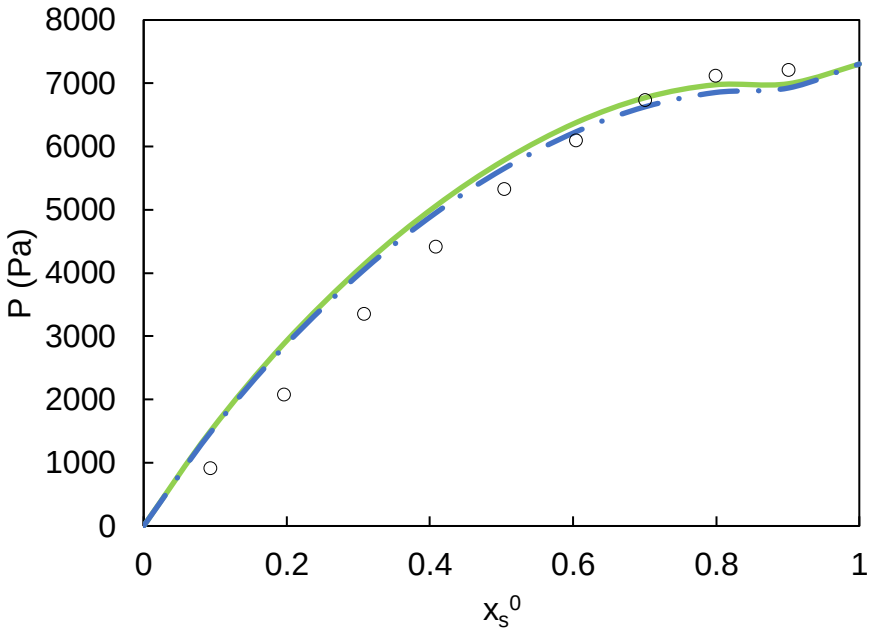
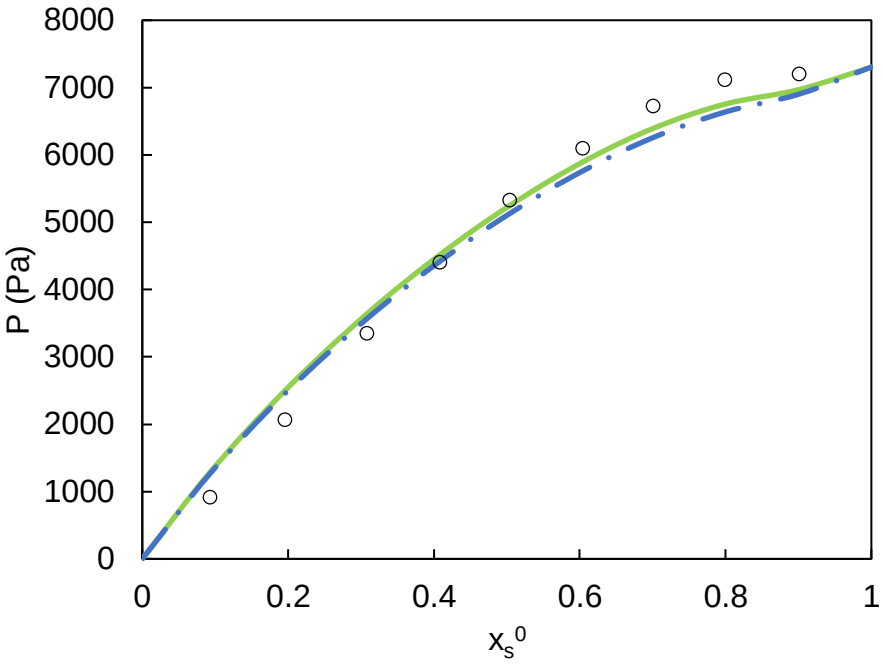


Fig. S3 The LLE of water mixed with [C_4MIM][PF_6] system[4]: (a) $\alpha = 1$ (b) $\alpha_0 = 0.35$ and (c) butanol mixed with [C_4MIM][TF_2N][5] with $\alpha = 1$ from different COSMO-SAC models (COSMO-SAC 2010: blue chain lines - · - · - ; COSMO-SAC 2018: green solid lines ——; experimental data: black circles ○)

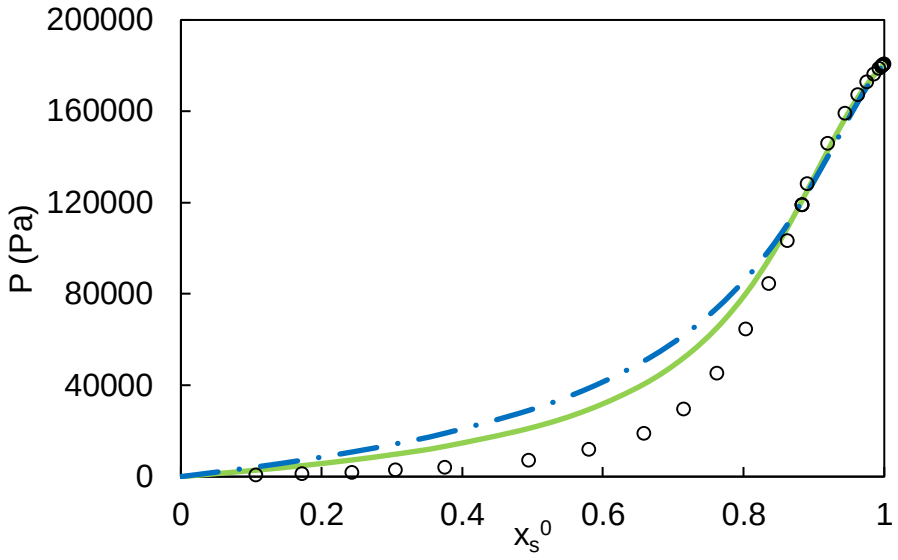
(a)



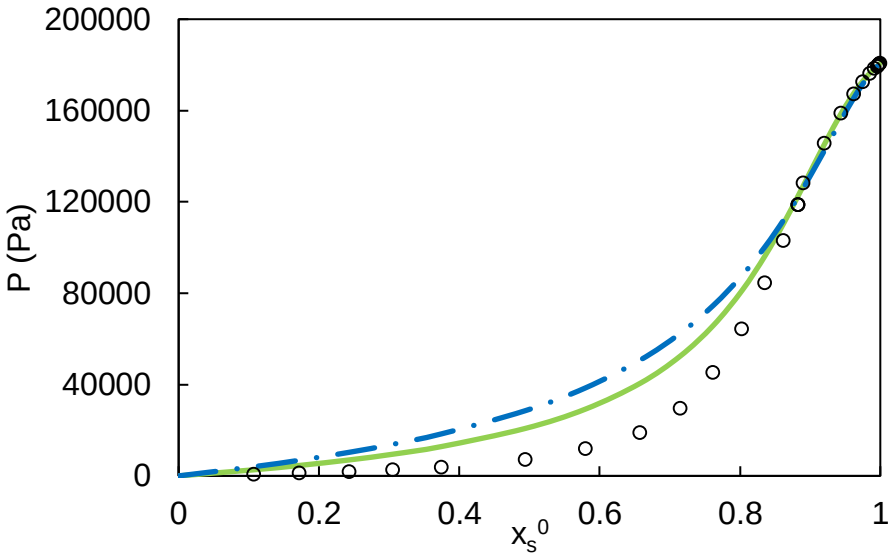
(b)



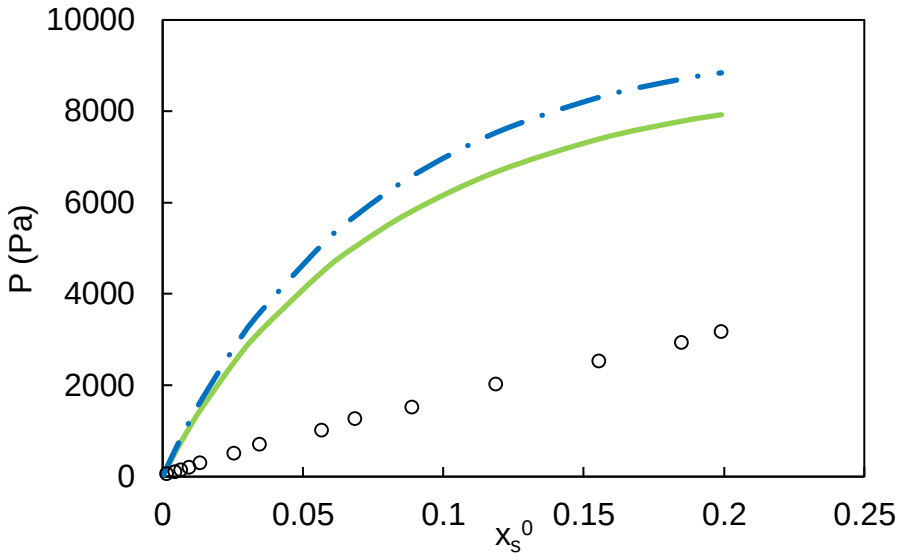
(c)


200000
160000
120000
80000
40000
0
P (Pa)
0
0.2
0.4
0.6
0.8
1
x_s^0

(d)


200000
160000
120000
80000
40000
0
P (Pa)
0
0.2
0.4
0.6
0.8
1
x_s^0

(e)



(f)

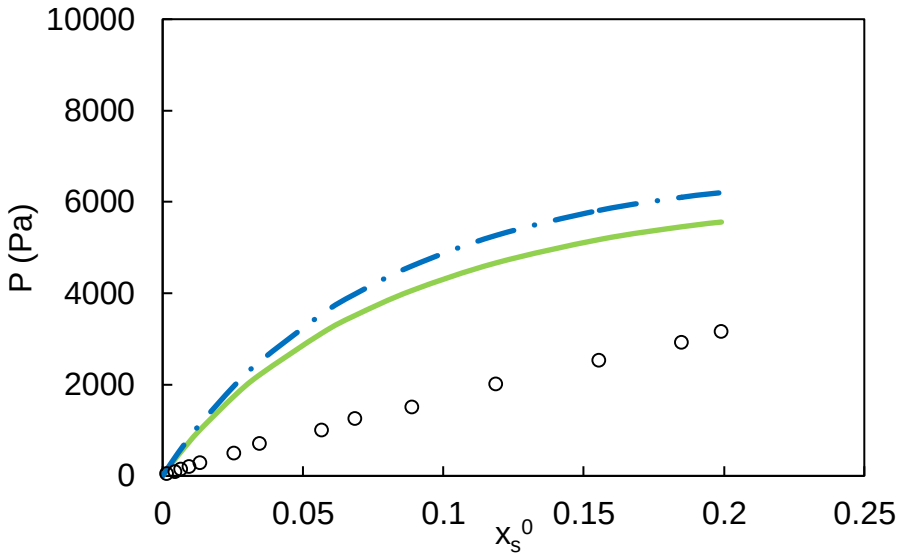


Fig. S4 The vapor pressure of methanol in [C_4MIM][BF_4] at 283.15 K[6] with $\alpha = 1$ (a) and $\alpha_0 = 0.35$ (b); methanol in [C_1MIM][DC_1Ph] at 353.15 K[7] with $\alpha = 1$ (c) and $\alpha_0 = 0.35$ (d); water in [C_8MIM][PF_6] at 298.15 K[8] with $\alpha = 1$ (e) and $\alpha_0 = 0.35$ (f) from the COSMO-SAC models and experimental data. (COSMO-SAC 2010: blue chain lines – · – ; COSMO-SAC 2018: green solid lines —— ; experimental data: black circles ○)

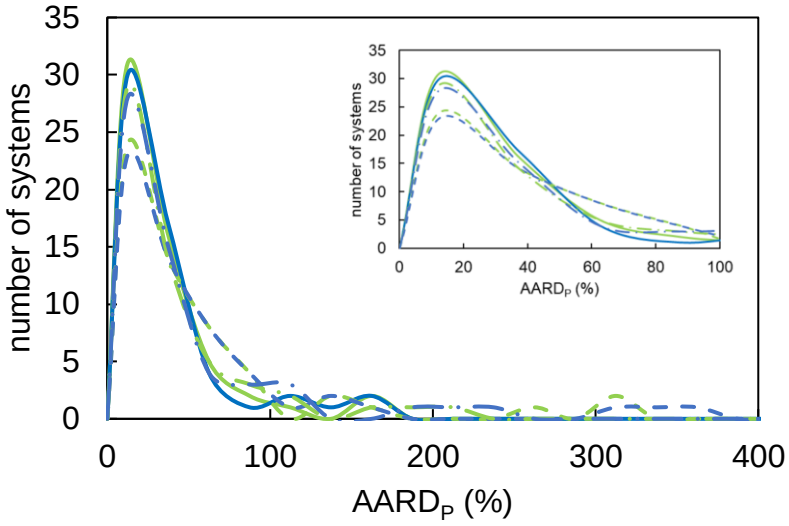


Fig. S5 Comparison of the distribution of AARD$_P$ in the VLE calculated from COSMO-SAC 2010 (blue lines ——)and COSMO-SAC 2018 (green lines ——) with different treatment of IL dissociation ($\alpha = 0$: solid lines ——; $\alpha_0 = 0.35$: chain lines — . —; $\alpha = 1$: dashed lines – – –)

S3. Details for determination of dielectric constant and density of individual species

For the PDH model, the density of a pure solvent is calculated from the molecular weight and its volume from COSMO calculations (V_i),[9] that is

$$d_i = \frac{M_i}{V_i N_a} \quad \text{(S1)}$$

where N_a is the Avogadro number.

The dielectric constant of a pure solvent is obtained by same method in the reference[10] for water (ϵ_{water}) with the following equation

$$\epsilon_{water} = 3.84093 \times 10^{-4} \times (T - 298.15)^2 - 3.18404 \times 10^{-1} \times (T - 298.15) + 78.3055 \quad \text{(S2)}$$

For other neutral molecules, cubic equation $\epsilon(\mathrm{T}) = a + b\mathrm{T} + c\mathrm{T}^2 + d\mathrm{T}^3$ is used with coefficients found in CRC handbook[11] . The empirical formula suggested by the reference is used for the ILs[12], which is

$$\epsilon_{IL} = 832.09 \times (1000 M_{IL})^{-0.701} \quad \text{(S3)}$$

Also note that for ionic liquid, both cation and anion are assumed to have same properties when using the extended PDH model (Eq. 2) That is,

$$\theta_{caion} = \theta_{anion} = \theta_{IL} \quad \text{(S4)}$$

where θ can be *M, d* or ϵ.

S4. Details for Determination of the Lone Pair Positions in the COSMO-SAC 2018

To make it easier for readers to reproduce the lone-pair position in the COMSO-SAC 2018 in ADF, we provide the calculation procedures and results of water molecule as an example. Once the readers who are interested in the determination of lone-pair positions or hbc can reproduce the results of water, they should also get right positions for the others. The first three rows are the input geometry of a water molecule. The local minima, which are the lone pair positions, are shown as E_1 and E_2. The direction of each lone pair is computed by subtracting E_i from O, the result is shown in the row $\overrightarrow{OE_1}$. Finally, the i-th $\overrightarrow{hbc}$ of water is determined by

$$\overrightarrow{hbc_i} = \vec{O} + \frac{\overrightarrow{OE_1}}{|\overrightarrow{OE_1}|} \times R_{COSMO}(O) \quad \text{(S5)}$$

where $R_{COSMO}(O)$ is the COSMO radius of O (= 1.72 Å).

Table S4. Input geometry of water, the LP positions obtained from ADF "densf" utility, and hbc used in the COSMO-SAC 2018.

	x (Å)	y (Å)	z (Å)
$\vec{O}$	0.00000	0.00000	0.59372
$\vec{H}$	0.00000	0.76544	-0.00836
$\vec{H}$	0.00000	-0.76544	-0.00836
$\overrightarrow{E_1}$	-0.95252	0.00000	1.40395
$\overrightarrow{E_2}$	0.95252	0.00000	1.40395
$\overrightarrow{OE_1}$	-0.95252	0.00000	0.81023
$\overrightarrow{OE_2}$	0.95252	0.00000	0.81023
$\overrightarrow{hbc_1}$	-1.31014	0.00000	1.70815
$\overrightarrow{hbc_2}$	1.31014	0.00000	1.70815

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