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Supporting Information

Modeling solubility of CO_2 gas in room temperature ionic liquids using COSMOSAC-LANL model: a first principles study

Anwesa Karmakar*[†] and Rangachary Mukundan*[‡]

[†]Theoretical Division (T-1), Los Alamos National Laboratory, Los Alamos 87545

[‡]MPA-11 Division, Los Alamos National Laboratory, Los Alamos 87545

E-mail: anwesak@lanl.gov; mukundan@lanl.gov

1 Derivation for Margules parameters used in the asymmetric solution model

The excess free energy of a binary solution can be written using 3-suffix Margules function[1,2]

$$G^{\text{ex}} = x_1 x_2 (A_{21} x_1 + A_{12} x_2) \tag{1}$$

where, x_1 and x_2 are the mole fractions for solute and solvent molecules in a binary mixture and A_{21} and A_{12} are the Margules parameters. The expression for total excess free energy for n total mole number of species is

$$nG^{\text{ex}} = \frac{n_1 n_2}{(n_1+n_2)^2}(A_{21}n_1 + A_{12}n_2)\,. \tag{2}$$

n_1 and n_2 are the number of moles of solute and solvent, respectively. Differentiating the above equation with respect to n_1, one will get,

$$\left(\frac{\partial n G^{\text{ex}}}{\partial n_1}\right)_{T,P,n_2} = RT\ln(\gamma_1) \tag{3}$$

$$\rightarrow RT\ln\gamma_1 = n_2\left[(A_{21}n_1 + A_{12}n_2)\left(\frac{1}{(n_1+n_2)^2} - \frac{2n_1}{(n_1+n_2)^3}\right) + \frac{n_1 A_{21}}{(n_1+n_2)^2}\right] \tag{4}$$

$$\rightarrow RT\ln\gamma_1 = \frac{n_2}{(n_1+n_2)}\left[\frac{(A_{21}n_1 + A_{12}n_2)}{(n_1+n_2)}\left(1 - \frac{2n_1}{(n_1+n_2)}\right) + \frac{n_1 A_{21}}{(n_1+n_2)}\right] \tag{5}$$

Reconversion of n_{i} to x_{i} will give

$$RT\ln\gamma_1 = x_2\left[(A_{21}x_1 + A_{12}x_2)(1-2x_1) + A_{21}x_1\right] \tag{6}$$

$$RT\ln\gamma_1 = x_2\left[(A_{21}x_1 + A_{12}x_2) - 2x_1(A_{21}x_1 + A_{12}x_2) + A_{21}x_1\right] \tag{7}$$

$$RT\ln\gamma_1 = x_2\left[2A_{21}x_1 + A_{12}x_2 - 2A_{21}x_1^2 - 2A_{12}x_1x_2\right] \tag{8}$$

As we know that : $x_1 = 1 - x_2$, therefore, we can write the above equation as

$$RT\ln\gamma_1 = x_2\left[2A_{21}x_1 + A_{12}x_2 - 2A_{21}x_1(1-x_2) - 2A_{12}x_1x_2\right] \tag{9}$$

$$RT\ln\gamma_1 = x_2^2\left[A_{12} + 2\left(A_{21} - A_{12}\right)x_1\right] \tag{10}$$

Subsituting $x_1 = 1 - x_2$ in the above equation, one will get

$$\rightarrow A_{12}x_2^2 + 2(A_{21} - A_{12})(x_2^2 - x_2^3) \tag{11}$$

$$\rightarrow A_{12}x_2^2 + \left(2A_{21}x_2^2 - 2A_{21}x_2^3 - 2A_{12}x_2^2 + 2A_{12}x_2^3\right) \tag{12}$$

Further simplifying the above equation one will get

$$RT\ln\gamma_1 = \left(2A_{21} - A_{12}\right)x_2^2 + \left(2A_{12} - 2A_{21}\right)x_2^3 \tag{13}$$

Now equating $\alpha_1 = \left(2A_{21} - A_{12}\right)$ and $\beta_1 = \left(2A_{12} - 2A_{21}\right)$, one can write Eq. 13 as

$$\ln\gamma_1 = \frac{\alpha_1 x_2^2 + \beta_1 x_2^3}{RT} \tag{14}$$

Similarly, for species 2, differentiating the above Eq. 1 with respect to n_2, one will get,

$$\left(\frac{\partial nG^{\text{ex}}}{\partial n_2}\right)_{T,P,n_1} = RT\ln(\gamma_2) \tag{15}$$

$$\rightarrow RT\ln\gamma_2 = n_1\left[(A_{21}n_1 + A_{12}n_2)\left(\frac{1}{(n_1+n_2)^2} - \frac{2n_2}{(n_1+n_2)^3}\right) + \frac{n_2A_{12}}{(n_1+n_2)^2}\right] \tag{16}$$

$$\rightarrow RT\ln\gamma_2 = \frac{n_1}{(n_1+n_2)}\left[\frac{(A_{21}n_1 + A_{12}n_2)}{(n_1+n_2)}\left(1 - \frac{2n_2}{(n_1+n_2)}\right) + \frac{n_2A_{12}}{(n_1+n_2)}\right] \tag{17}$$

Reconversion of n_{i} to x_{i} will give

$$RT\ln\gamma_2 = x_1\left[(A_{21}x_1 + A_{12}x_2)(1 - 2x_2) + A_{12}x_2\right] \tag{18}$$

$$RT\ln\gamma_2 = x_1\left[(A_{21}x_1 + A_{12}x_2) - 2x_2(A_{21}x_1 + A_{12}x_2) + A_{12}x_2\right] \tag{19}$$

$$RT\ln\gamma_2 = x_1\left[2A_{12}x_2 + A_{21}x_1 - 2A_{12}x_2^2 - 2A_{21}x_1x_2\right] \tag{20}$$

As we know that : $x_2 = 1 - x_1$, therefore, we can write the above equation as

$$RT\ln\gamma_2 = x_1\left[2A_{12}x_2 + A_{21}x_1 - 2A_{12}x_2(1 - x_1) - 2A_{21}x_1x_2\right] \tag{21}$$

$$RT\ln\gamma_2 = x_1^2\Bigg[A_{21} + 2\Bigg(A_{12} - A_{21}\Bigg)x_2\Bigg] \tag{22}$$

Substituting $x_2 = 1 - x_1$ in the above equation, one will get

$$\rightarrow A_{21}x_1^2 + 2(A_{12} - A_{21})(x_1^2 - x_1^3) \tag{23}$$

$$\rightarrow A_{21}x_2^2 + \Bigg(2A_{12}x_1^2 - 2A_{12}x_1^3 - 2A_{21}x_1^2 + 2A_{21}x_1^3\Bigg) \tag{24}$$

Further simplifying of the above equation one will get

$$RT\ln\gamma_2 = \Bigg(2A_{12} - A_{21}\Bigg)x_1^2 + \Bigg(2A_{21} - 2A_{12}\Bigg)x_1^3 \tag{25}$$

Now equating $\alpha_2 = \Bigg(2A_{12} - A_{21}\Bigg)$ and $\beta_2 = \Bigg(2A_{21} - 2A_{12}\Bigg)$, one can write Eq. 25 as

$$\ln\gamma_2 = \frac{\alpha_2 x_1^2 + \beta_2 x_1^3}{RT}\,. \tag{26}$$

2 Derivation of 2-suffix Margules function from 3-suffix Margules function

At $x_1 \longrightarrow 0$ and $x_2 \longrightarrow 1$, the above Eq. 1 will be reduced to

$$\frac{G^{\mathrm{ex}}}{x_1x_2} = A_{12}\,. \tag{27}$$

At $x_2 \longrightarrow 0$ and $x_1 \longrightarrow 1$, the above eq. (1) will be reduced to

$$\frac{G^{\mathrm{ex}}}{x_1x_2} = A_{21}\,. \tag{28}$$

If one replaces A_{12} and A_{21} by A, when they are equal to each other ($\mathrm{A}_{12} = \mathrm{A}_{21}$). They represent the symmetric interactions between the solute and solvent molecules. The Eqs. 27 and 28 will be reduced to

$$\frac{G^{\mathrm{ex}}}{x_1x_2} = A\,. \tag{29}$$

The above equation is known as the 2-suffix Margules function. The expression for total excess free energy for n total mole number of species is

$$nG^{\mathrm{ex}} = \frac{An_1n_2}{(n_1 + n_2)}\,, \tag{30}$$

where, n_1 and n_2 are the number of moles of solute and solvent, respectively. Differentiating the above equation with respect to n_1, one will get,

$$\left(\frac{\partial nG^{\text{ex}}}{\partial n_1}\right)_{T,P,n_2} = RT\ln(\gamma_1) \tag{31}$$

$$\rightarrow RT\ln\gamma_1 = A\left(\frac{n_2}{n_1+n_2} - \frac{n_1 n_2}{(n_1+n_2)^2}\right) \tag{32}$$

$$\rightarrow RT\ln\gamma_1 = Ax_2^2 \tag{33}$$

Similarly, it can be derived for species 2 as

$$RT\ln\gamma_2 = Ax_1^2\,. \tag{34}$$

The Eqs. 33 and 34 are symmetric function and correspond to the symmetric interaction between the solute and solvent molecules.

3 Staverman-Guggenheim combinatorial term

The Staverman-Guggenheim (SG)[3–5] combinatorial term is based on the Flory-Huggins model, however the SG term also consider the interaction between the solute and solvent species due their shape differences to some extent. The combinatorial term proposed in the UNIQUAC model was

$$\frac{g^E(COMB)}{RT} = x_1\ln\frac{\phi_1}{x_1} + x_2\ln\frac{\phi_2}{x_2} + \frac{z}{2}\left(q_1x_1\ln\frac{\phi_1}{x_1} + q_2x_2\ln\frac{\phi_2}{x_2}\right) \tag{35}$$

for the binary mixture system using the local composition theory. z is the coordination number equal to 10. The fraction volume (ϕ_{i}) and surface area (θ_{i}) are as

$$\phi_{\text{i}} = \frac{x_{\text{i}}r_{\text{i}}}{\sum_{j=1}^{2} x_{\text{j}}r_{\text{j}}} \;\text{ and }\; \theta_{\text{i}} = \frac{x_{\text{i}}q_{\text{i}}}{\sum_{j=1}^{2} x_{\text{j}}q_{\text{j}}}\;, \text{respectively}\,, \tag{36}$$

where, r_{i} and q_{i} are the normalized volume and surface area of species i=1,2.

The activity coefficient will be obtained from the above expression[6]

$$\left(\frac{\partial nG^{\text{ex}}}{\partial n_{\text{i}}}\right)_{T,P,n_{\text{i}\neq\text{j}}} = RT\ln(\gamma_{\text{i}}) \tag{37}$$

for the species i=1,2. The Staverman-Guggenheim (SG) combinatorial for solute and solvent species is

$$\ln(\gamma_{\mathrm{i/S}}^{\mathrm{comb}}) = 1 - \frac{\phi_{\mathrm{i}}}{x_{\mathrm{i}}} + \ln\frac{\phi_{\mathrm{i}}}{x_{\mathrm{i}}} - \frac{z}{2}q_{\mathrm{i}}\left(1 - \frac{\phi_{\mathrm{i}}}{\theta_{\mathrm{i}}} + \ln\frac{\phi_{\mathrm{i}}}{\theta_{\mathrm{i}}}\right). \tag{38}$$

For solute species(1), one can write the above equation as

$$\ln(\gamma_{\mathrm{1/S}}^{\mathrm{comb}}) = 1 - \frac{\phi_1}{x_1} + \ln\frac{\phi_1}{x_1} - \frac{z}{2}q_1\left(1 - \frac{\phi_1}{\theta_1} + \ln\frac{\phi_1}{\theta_1}\right) \tag{39}$$

where, the fraction volume (ϕ_1) and surface area (θ_1) are as

$$\phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \text{ and } \theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}\text{ , respectively },\tag{40}$$

where, r_1 and q_1 are the normalized volume and surface area of solute, respectively, while r_2 and q_2 are the normalized volume and surface area for solvent species, respectively. x_1 and x_2 are the mole fractions of solute and solvent species, respectively. Now suppose r_1' and q_1' are the unnormalized volume and surface area for solute species obtained from COSMO calculations, then one can write $r_1 = \frac{r_1'}{r_0}$ and $q_1 = \frac{q_1'}{q_0}$, where r_0 and q_0 are 66.69 $\mathrm{\AA}^3$ and 79.53 $\mathrm{\AA}^2$, respectively. Now, if one substitute r_1 and q_1 in Eq. 40, one will get

$$\phi_1 = \frac{x_1 r_1'/r_0}{x_1 r_1'/r_0 + x_2 r_2'/r_0} \text{ and } \theta_1 = \frac{x_1 q_1'/q_0}{x_1 q_1'/q_0 + x_2 q_2'/q_0}\text{ , respectively }.\tag{41}$$

Therefore,

$$\phi_1 = \frac{x_1 r_1'}{x_1 r_1' + x_2 r_2'} \text{ and } \theta_1 = \frac{x_1 q_1'}{x_1 q_1' + x_2 q_2'}\text{ , respectively }.\tag{42}$$

Now if one substitutes ϕ_1, θ_1 and q_1 in the Eq. 39, one will obtain

$$\ln(\gamma_{\mathrm{1/S}}^{\mathrm{comb}}) = 1 - \left(\frac{\frac{x_1 r_1'}{x_1 r_1' + x_2 r_2'}}{x_1}\right) + \ln\left(\frac{\frac{x_1 r_1'}{x_1 r_1' + x_2 r_2'}}{x_1}\right) - \frac{z}{2}\frac{q_1'}{q_0}\left[1 - \left(\frac{\frac{x_1 r_1'}{x_1 r_1' + x_2 r_2'}}{\frac{x_1 q_1'}{x_1 q_1' + x_2 q_2'}}\right) + \ln\left(\frac{\frac{x_1 r_1'}{x_1 r_1' + x_2 r_2'}}{\frac{x_1 q_1'}{x_1 q_1' + x_2 q_2'}}\right)\right]. \tag{43}$$

By simplifying, the above equation can be written as

$$\ln(\gamma_{\mathrm{1/S}}^{\mathrm{comb}}) = 1 - \left(\frac{r_1'}{x_1 r_1' + x_2 r_2'}\right) + \ln\left(\frac{r_1'}{x_1 r_1' + x_2 r_2'}\right) - \frac{z}{2}\frac{q_1'}{q_0}\left[1 - \left(\frac{\frac{r_1'}{x_1 r_1' + x_2 r_2'}}{\frac{q_1'}{x_1 q_1' + x_2 q_2'}}\right) + \ln\left(\frac{\frac{r_1'}{x_1 r_1' + x_2 r_2'}}{\frac{q_1'}{x_1 q_1' + x_2 q_2'}}\right)\right]. \tag{44}$$

Similarly, one can write this expression for solvent species,

$$\ln(\gamma_{2/\mathrm{S}}^{\mathrm{comb}}) = 1-\left(\frac{r_2'}{x_1r_1'+x_2r_2'}\right)+\ln\left(\frac{r_2'}{x_1r_1'+x_2r_2'}\right)-\frac{z}{2}\frac{q_2'}{q_0}\left[1-\left(\frac{\frac{r_2'}{x_1r_1'+x_2r_2'}}{\frac{q_2'}{x_1q_1'+x_2q_2'}}\right)+\ln\left(\frac{\frac{r_2'}{x_1r_1'+x_2r_2'}}{\frac{q_2'}{x_1q_1'+x_2q_2'}}\right)\right]. \tag{45}$$

The above two expressions are very similar to the expression of SG term used in COSMOSAC-LANL model.

4 Binary and ternary mixture treatment[7] in COSMOSAC-LANL model

If the ionic liquid is treated as separate cation and anion within the COSMO-RS framework in COSMOSAC model, the mole fraction of the solute species (i) is

$$x_{i/S}^{\text{separate}} = \frac{n_i}{n_i + n_{cation} + n_{anion}}. \tag{46}$$

Experimental mole fraction is based on IL

$$x_{i/S}^{\text{together}} = \frac{n_i}{n_i + n_{IL}}. \tag{47}$$

Suppose the activity coefficient resulted from the separate cation and anion treatment of the ionic liquid, the activity coefficient will be $\gamma_{i/S}^{\text{separate}}$ which will be related to the $\gamma_{i/S}^{\text{together}}$ which is the activity coefficient of the ionic liquid when they are treated as a single molecule. Therefore,

$$\gamma_{i/S}^{\text{together}} = \frac{x_{i/S}^{\text{separate}}.\gamma_{i/S}^{\text{separate}}}{x_i^{\text{together}}} \tag{48}$$

For an univalent IL ($n_i = n_{cation} = n_{anion}$) and for an infinite dilution of solute ($n_i \longrightarrow 0$), the above Eq. 48 will be reduced to

$$\gamma_{i/S}^{\text{together}} = \frac{(n_i + n_{IL}).\gamma_i^{\text{separate}}}{n_i + 2.n_{IL}} \tag{49}$$

$$\gamma_{i/S}^{\text{together}} = \frac{\gamma_{i/S}^{\text{separate}}}{2}, \tag{50}$$

where, $\gamma_{i/S}^{\text{separate}}$ is the activity coefficient of the solute in a ternary mixture at the infinite dilute condition and $\gamma_{i/S}^{\text{together}}$ is the activity coefficient of the solute in a binary mixture at the infinite dilute condition.

5 Analytical solution of thermodynamic consistency of 3-suffix Margules function for activity coefficient

An activity coefficient model must obey Gibbs-Duhem relation

$$x_1 \mathrm{d}\ln\gamma_1 + x_2 \mathrm{d}\ln\gamma_2 = 0\,, \tag{51}$$

where, x_1 and x_2 are the mole fraction of solute (1) and solvent (2) species, respectively and γ_1 and γ_2 are the activity coefficient of solute and solvent, respectively. Now, we already know, the expression of asymmetric activity coefficient for solute species is

$$\ln\gamma_1 = \Bigg(2A_{21} - A_{12}\Bigg)x_2^2 + \Bigg(2A_{12} - 2A_{21}\Bigg)x_2^3\,, \tag{52}$$

and for solvent, the expression is

$$\ln\gamma_2 = \Bigg(2A_{12} - A_{21}\Bigg)x_1^2 + \Bigg(2A_{21} - 2A_{12}\Bigg)x_1^3. \tag{53}$$

From Eq. 52 one will get for solute,

$$\mathrm{d}\ln\gamma_1 = \Bigg[\Bigg(2A_{21} - A_{12}\Bigg)2x_2 + \Bigg(2A_{12} - 2A_{21}\Bigg)3x_2^2\Bigg]\mathrm{d}x_2\,, \tag{54}$$

and from Eq. 53 one will get for solvent,

$$\mathrm{d}\ln\gamma_2 = \Bigg[\Bigg(2A_{12} - A_{21}\Bigg)2x_1 + \Bigg(2A_{21} - 2A_{12}\Bigg)3x_1^2\Bigg]\mathrm{d}x_2\,. \tag{55}$$

Now, after adding Eqs. 54 and 55, and multiplying each equation by x_1 and x_2, respectively, one will get,

$$\begin{aligned} x_1 \mathrm{d}\ln\gamma_1 + x_2 \mathrm{d}\ln\gamma_2 = &\Bigg[\Bigg(2A_{21} - A_{12}\Bigg)2x_2x_1 + \Bigg(2A_{12} - 2A_{21}\Bigg)3x_2^2x_1\Bigg]\mathrm{d}x_2 + \\ &\Bigg[\Bigg(2A_{12} - A_{21}\Bigg)2x_1x_2 + \Bigg(2A_{21} - 2A_{12}\Bigg)3x_1^2x_2\Bigg]\mathrm{d}x_2 \end{aligned} \tag{56}$$

Now we have, $x_1 + x_2 = 1 \implies x_1 = (1 - x_2) \implies \mathrm{d}x_1 = -\mathrm{d}x_2$, substituting this into above equation one will get,

$$\implies \Bigg[6A_{21}x_1x_2 - 6A_{12}x_1x_2 - 6A_{21}x_1x_2 + 6A_{12}x_1x_2\Bigg]\mathrm{d}x_2 = 0\,. \tag{57}$$

Therefore, Gibbs-Duhem relation is satisfied by the model

$$x_1 \mathrm{d}\ln\gamma_1 + x_2 \mathrm{d}\ln\gamma_2 = 0\,. \tag{58}$$

6 Validation of Gibbs-Duhem relationship for COSMOSAC-LANL model

We have already mentioned that a good activity coefficient model is needed to obey the Gibbs-Duhem relationship. Here, we have validated our model for the two binary mixture models: (i) CO_2 in $[C_4mim][NTf_2]$ and (ii) CH_4 in $[C_4mim][NTf_2]$ at 298 K. We have used the central method for numerical differentiation. They are discussed in next few lines.

If a variable y depends on the another variable x, i.e. $y = f(x)$, but we only know the f at a finite set of points such as $(x_1; y_1); (x_2; y_2); \cdots\cdots; (x_n; y_n)$. To obtain the derivative of $f(x)$, one can do central numerical differentiation

$$f'(x) = \frac{y_{i+1} - y_{i-1}}{2(x_{i+1} - x_{i-1})} \,. \tag{59}$$

We have shown that the GD relationship is obeyed by the activity coefficient model for both systems. The results are given in the following tables.

Table S 1: Gibbs-Duhem relationship from COSMOSAC-LANL model for (i) CO_2 in [C_4mim][NTf_2] and (ii) CH4 in [C_4mim][NTf_2] at 298 K.

The calculation is $x_1 \frac{\partial \ln\gamma_1}{\partial x_1} + x_2 \frac{\partial \ln\gamma_2}{\partial x_2}$.

	CO_2	[C_4mim][NTf_2]		CH4	[C_4mim][NTf_2]	
x_1 (mole fraction)	$\ln\gamma_1$	$\ln\gamma_2$	GD	$\ln\gamma_1$	$\ln\gamma_2$	GD
5.00E-03	0.873	1.000	3.23E-04	-0.535	1.000	-7.30E-03
1.50E-02	0.871	1.001	3.40E-04	-0.530	1.000	2.66E-06
2.50E-02	0.869	1.002	3.56E-04	-0.524	1.000	4.92E-06
3.50E-02	0.868	1.005	3.72E-04	-0.518	1.000	7.58E-06
4.50E-02	0.867	1.008	3.88E-04	-0.512	1.000	1.06E-05
5.50E-02	0.867	1.012	4.03E-04	-0.505	0.999	1.41E-05
6.50E-02	0.868	1.016	4.18E-04	-0.498	0.999	1.79E-05
7.50E-02	0.869	1.021	4.32E-04	-0.491	0.998	2.21E-05
8.50E-02	0.870	1.027	4.46E-04	-0.484	0.998	2.66E-05
9.50E-02	0.872	1.033	4.59E-04	-0.476	0.997	3.15E-05
0.105	0.875	1.040	4.71E-04	-0.468	0.996	3.67E-05
0.115	-0.565	1.047	4.82E-04	-0.459	0.995	4.22E-05
0.125	-0.521	1.055	4.92E-04	-0.450	0.993	4.81E-05
0.135	-0.476	1.063	5.01E-04	-0.441	0.992	5.43E-05
0.145	-0.431	1.072	-7.29E-03	-0.432	0.990	6.07E-05
0.155	-0.385	1.081	-1.00E-05	-0.423	0.988	6.75E-05
0.165	-0.338	1.091	-1.52E-05	-0.413	0.985	7.45E-05
0.175	-0.290	1.102	-1.93E-05	-0.403	0.983	8.18E-05
0.185	-0.243	1.112	-2.24E-05	-0.392	0.980	8.94E-05
0.195	-0.195	1.123	-2.47E-05	-0.381	0.977	9.72E-05
0.205	-0.147	1.135	-2.61E-05	-0.370	0.973	1.05E-04
0.215	-0.099	1.146	-2.68E-05	-0.359	0.969	1.14E-04
0.225	-0.051	1.158	-2.70E-05	-0.348	0.965	1.22E-04
0.235	-0.003	1.171	-2.67E-05	-0.336	0.960	1.31E-04
0.245	0.044	1.183	-2.59E-05	-0.324	0.955	1.40E-04
0.255	0.091	1.196	-2.49E-05	-0.312	0.950	1.49E-04
0.265	0.138	1.209	-2.37E-05	-0.299	0.944	1.58E-04
0.275	0.183	1.222	-2.23E-05	-0.286	0.937	1.68E-04
0.285	0.228	1.235	-2.08E-05	-0.273	0.930	1.77E-04
0.295	0.272	1.248	-1.93E-05	-0.260	0.923	1.87E-04
0.305	0.315	1.261	-1.79E-05	-0.246	0.915	1.97E-04
0.315	0.357	1.274	-1.66E-05	-0.232	0.907	2.07E-04
0.325	0.398	1.287	-1.54E-05	-0.218	0.898	2.17E-04

	CO_2	[C_4mim][NTf_2]		CH4	[C_4mim][NTf_2]	
x_1 (mole fraction)	lnγ_1	lnγ_2	GD	lnγ_1	lnγ_2	GD
0.335	0.438	1.300	-1.45E-05	-0.203	0.888	2.28E-04
0.345	0.476	1.312	-1.37E-05	-0.188	0.878	2.38E-04
0.355	0.513	1.325	-1.32E-05	-0.173	0.868	2.48E-04
0.365	0.548	1.337	-1.30E-05	-0.158	0.857	2.59E-04
0.375	0.582	1.349	-1.31E-05	-0.143	0.845	2.70E-04
0.385	0.614	1.360	-1.34E-05	-0.127	0.832	2.80E-04
0.395	0.645	1.371	-1.40E-05	-0.111	0.819	2.91E-04
0.405	0.674	1.381	-1.48E-05	-0.094	0.805	3.02E-04
0.415	0.701	1.390	-1.58E-05	-0.078	0.791	3.12E-04
0.425	0.727	1.399	-1.71E-05	-0.061	0.776	3.23E-04
0.435	0.751	1.407	-1.85E-05	-0.044	0.760	3.34E-04
0.445	0.774	1.414	-2.00E-05	-0.026	0.743	3.44E-04
0.455	0.795	1.420	-2.15E-05	-0.009	0.726	3.55E-04
0.465	0.814	1.425	-2.31E-05	0.009	0.708	3.66E-04
0.475	0.831	1.429	-2.46E-05	0.027	0.689	3.76E-04
0.485	0.847	1.431	-2.61E-05	0.045	0.669	3.86E-04
0.495	0.862	1.433	-2.73E-05	0.064	0.648	3.97E-04
0.505	0.875	1.432	-2.84E-05	0.083	0.627	4.07E-04
0.515	0.886	1.430	-2.92E-05	0.102	0.605	4.17E-04
0.525	0.896	1.427	-2.96E-05	0.121	0.582	4.27E-04
0.535	0.905	1.421	-2.97E-05	0.141	0.558	4.37E-04
0.545	0.913	1.414	-2.93E-05	0.161	0.533	4.47E-04
0.555	0.919	1.405	-2.83E-05	0.180	0.507	4.56E-04
0.565	0.924	1.394	-2.68E-05	0.201	0.480	4.66E-04
0.575	0.928	1.380	-2.47E-05	0.221	0.453	4.75E-04
0.585	0.931	1.365	-2.20E-05	0.242	0.424	4.84E-04
0.595	0.933	1.346	-1.85E-05	0.262	0.394	4.93E-04
0.605	0.934	1.326	-1.44E-05	0.283	0.363	5.02E-04
0.615	0.935	1.302	-9.41E-06	0.304	0.331	5.10E-04
0.625	0.934	1.276	-3.69E-06	0.325	0.298	5.18E-04
0.635	0.933	1.247	2.82E-06	0.347	0.264	5.26E-04
0.645	0.931	1.215	1.01E-05	0.368	0.229	5.34E-04
0.655	0.929	1.180	1.83E-05	0.390	0.192	5.42E-04
0.665	0.926	1.142	2.72E-05	0.412	0.154	5.49E-04
0.675	0.923	1.100	3.69E-05	0.433	0.114	5.56E-04
0.685	0.920	1.055	4.74E-05	0.455	0.074	5.62E-04
0.695	0.916	1.006	5.87E-05	0.477	0.031	5.68E-04
0.705	0.912	0.954	7.07E-05	0.499	-0.013	5.74E-04

	CO_2	$[C_4mim][NTf_2]$		CH4	$[C_4mim][NTf_2]$	
x_1 (mole fraction)	lnγ_1	lnγ_2	GD	lnγ_1	lnγ_2	GD
0.715	0.908	0.897	8.34E-05	0.521	-0.058	5.80E-04
0.725	0.904	0.837	9.67E-05	0.543	-0.106	5.85E-04
0.735	0.900	0.773	1.11E-04	0.565	-0.155	5.89E-04
0.745	0.896	0.704	1.25E-04	0.587	-0.206	5.93E-04
0.755	0.892	0.631	1.40E-04	0.609	-0.259	5.97E-04
0.765	0.888	0.553	1.56E-04	0.631	-0.315	5.99E-04
0.775	0.884	0.471	1.72E-04	0.652	-0.373	6.02E-04
0.785	0.881	0.383	1.88E-04	0.674	-0.433	6.03E-04
0.795	0.878	0.290	2.04E-04	0.695	-0.497	6.04E-04
0.805	0.875	0.191	2.21E-04	0.717	-0.563	6.04E-04
0.815	0.879	0.087	2.38E-04	0.738	-0.632	6.03E-04
0.825	0.883	-0.024	2.55E-04	0.758	-0.705	6.00E-04
0.835	0.887	-0.141	2.72E-04	0.779	-0.782	5.97E-04
0.845	0.893	-0.266	2.89E-04	0.799	-0.863	5.92E-04
0.855	0.898	-0.399	3.06E-04	0.818	-0.948	5.86E-04
0.865	0.905	-0.539	5.08E-04	0.837	-1.039	5.77E-04
0.875	0.912	-0.690	5.13E-04	0.856	-1.134	5.67E-04
0.885	0.919	-0.850	5.16E-04	0.874	-1.236	5.54E-04
0.895	0.927	-1.021	5.17E-04	0.891	-1.345	5.38E-04
0.905	0.935	-1.204	5.13E-04	0.908	-1.460	5.19E-04
0.915	0.944	-1.402	5.06E-04	0.923	-1.584	4.96E-04
0.925	0.952	-1.615	4.93E-04	0.938	-1.717	4.68E-04
0.935	0.961	-1.845	4.74E-04	0.952	-1.859	4.35E-04
0.945	0.970	-2.095	4.46E-04	0.964	-2.013	3.96E-04
0.955	0.978	-2.368	4.08E-04	0.975	-2.179	3.49E-04
0.965	0.985	-2.668	3.55E-04	0.984	-2.360	2.93E-04
0.975	0.992	-2.998	2.85E-04	0.992	-2.556	2.26E-04
0.985	0.997	-3.364	1.93E-04	0.997	-2.770	1.47E-04
0.995	1.000	-3.771	9.65E-03	1.000	-3.003	8.18E-03

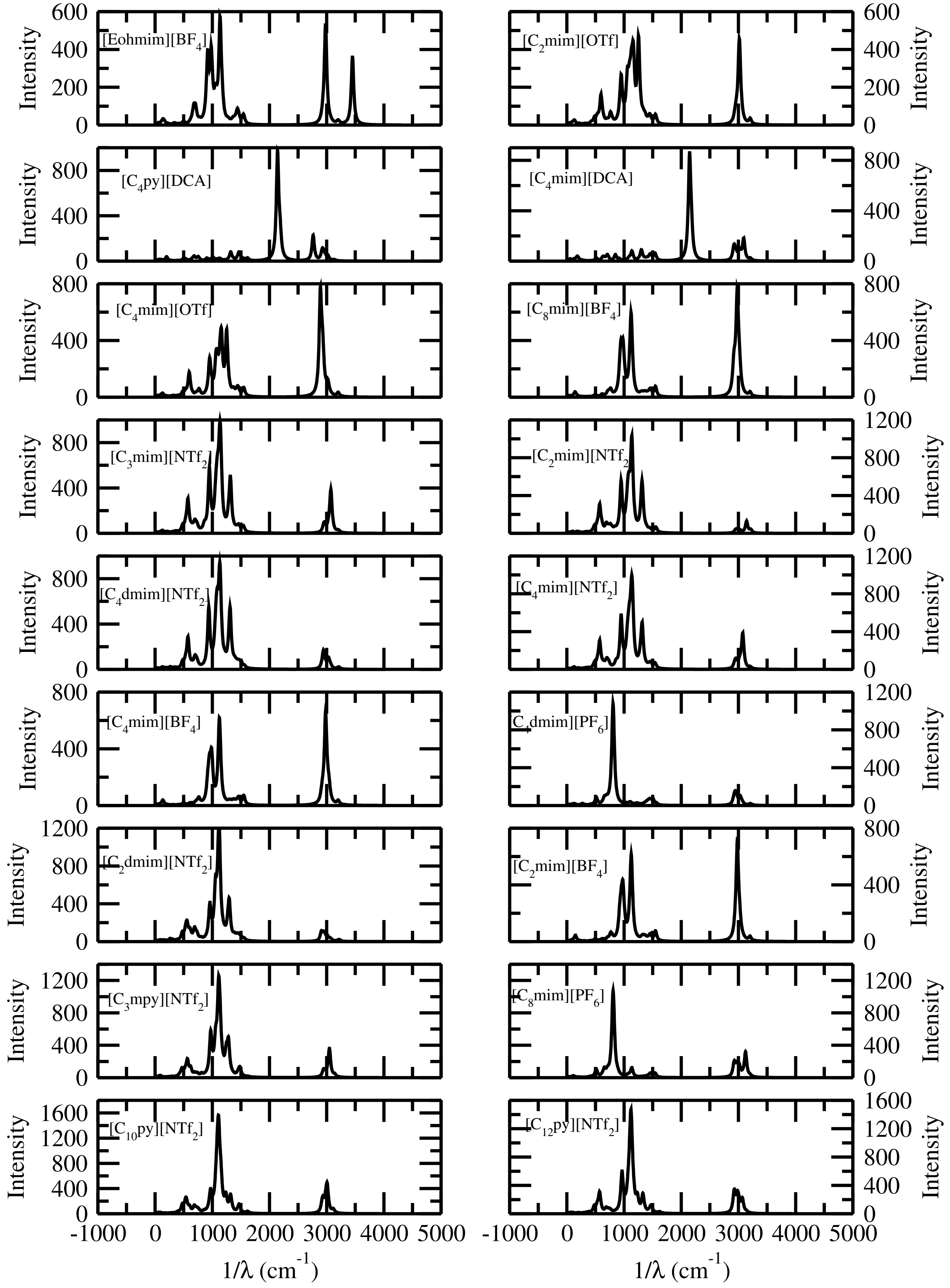


Figure. S 1: Analytical frequency of selected 18 ionic liquids at room temperature.

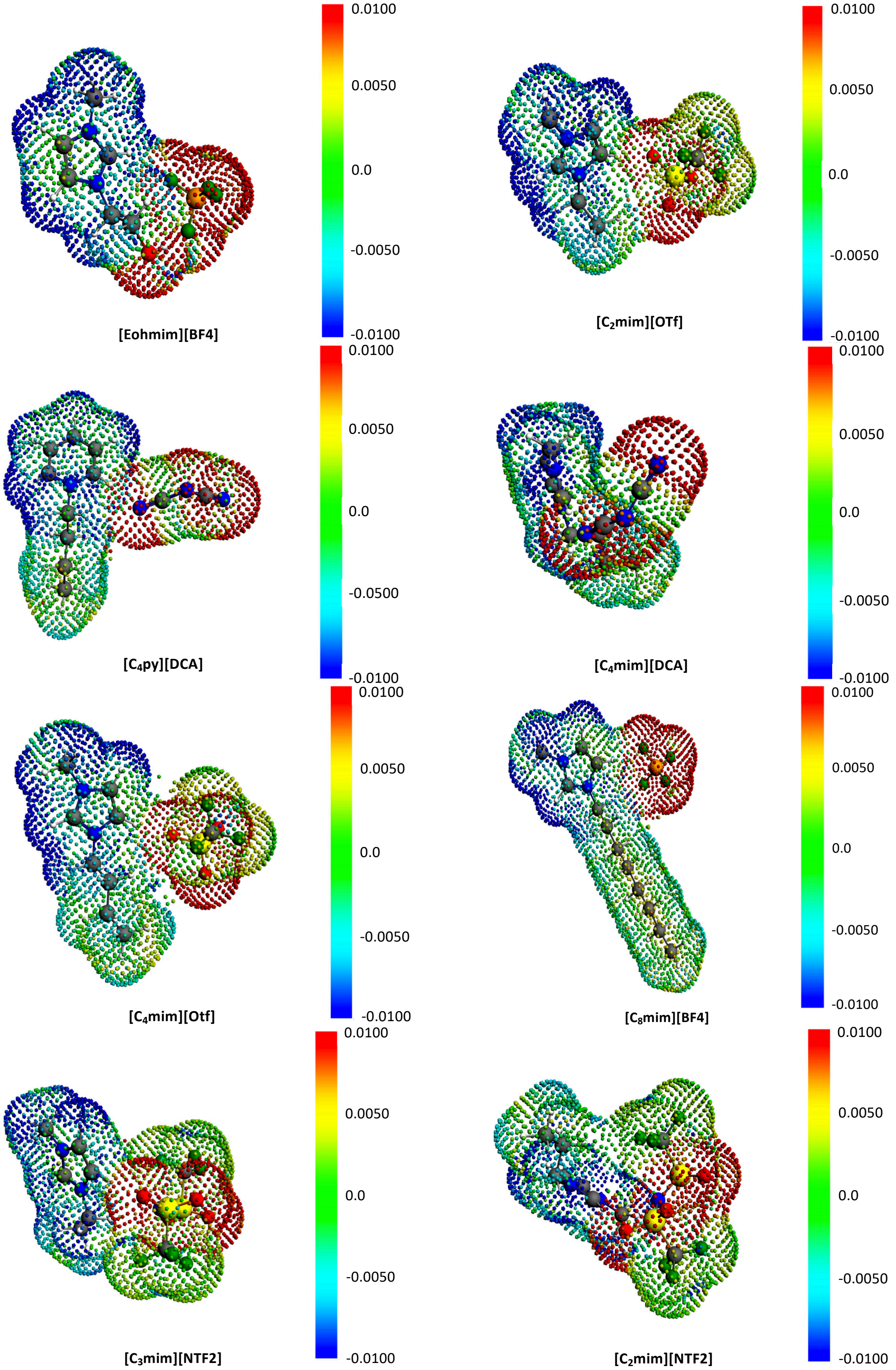


Figure. S 2: COSMO surface points of certain ionic liquids.

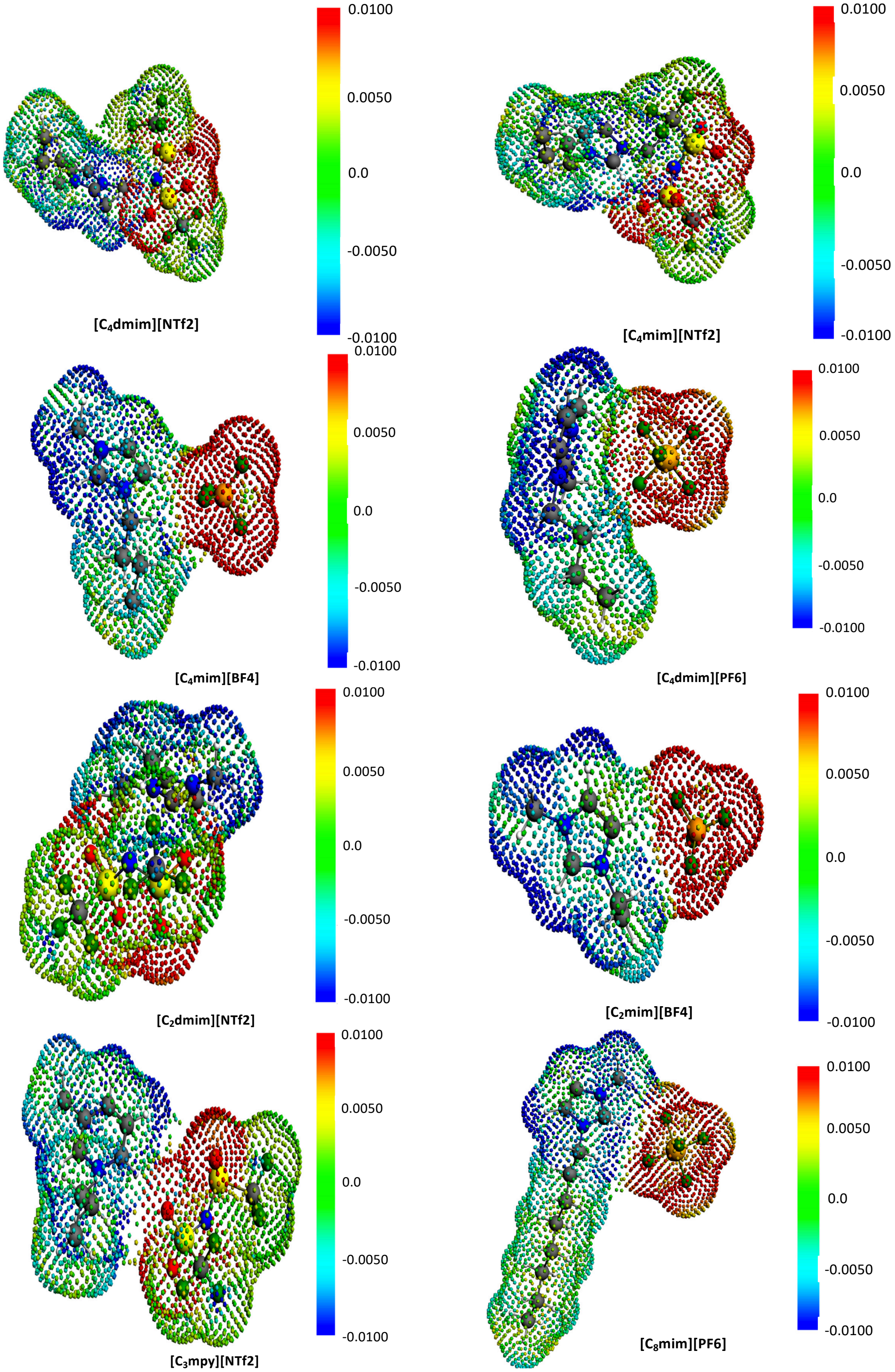
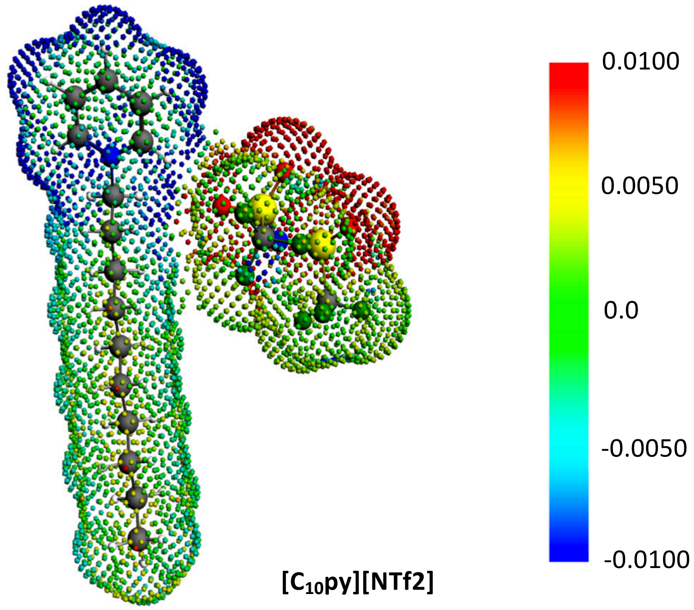
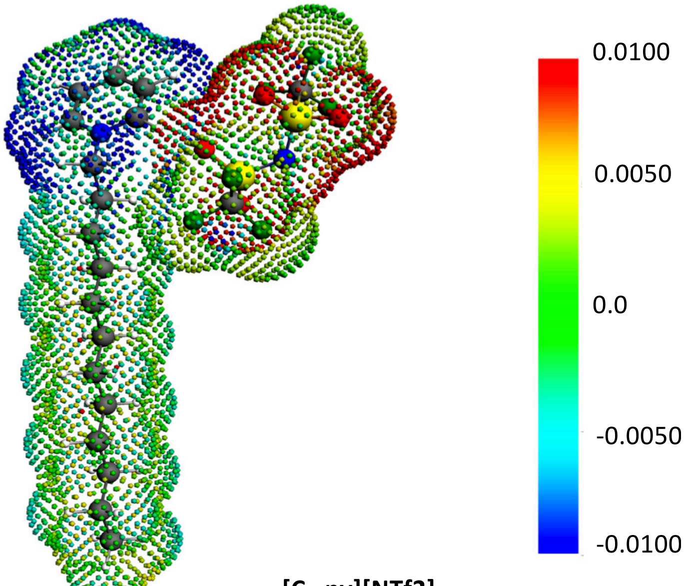


Figure. S 3: COSMO surface points of certain ionic liquids.

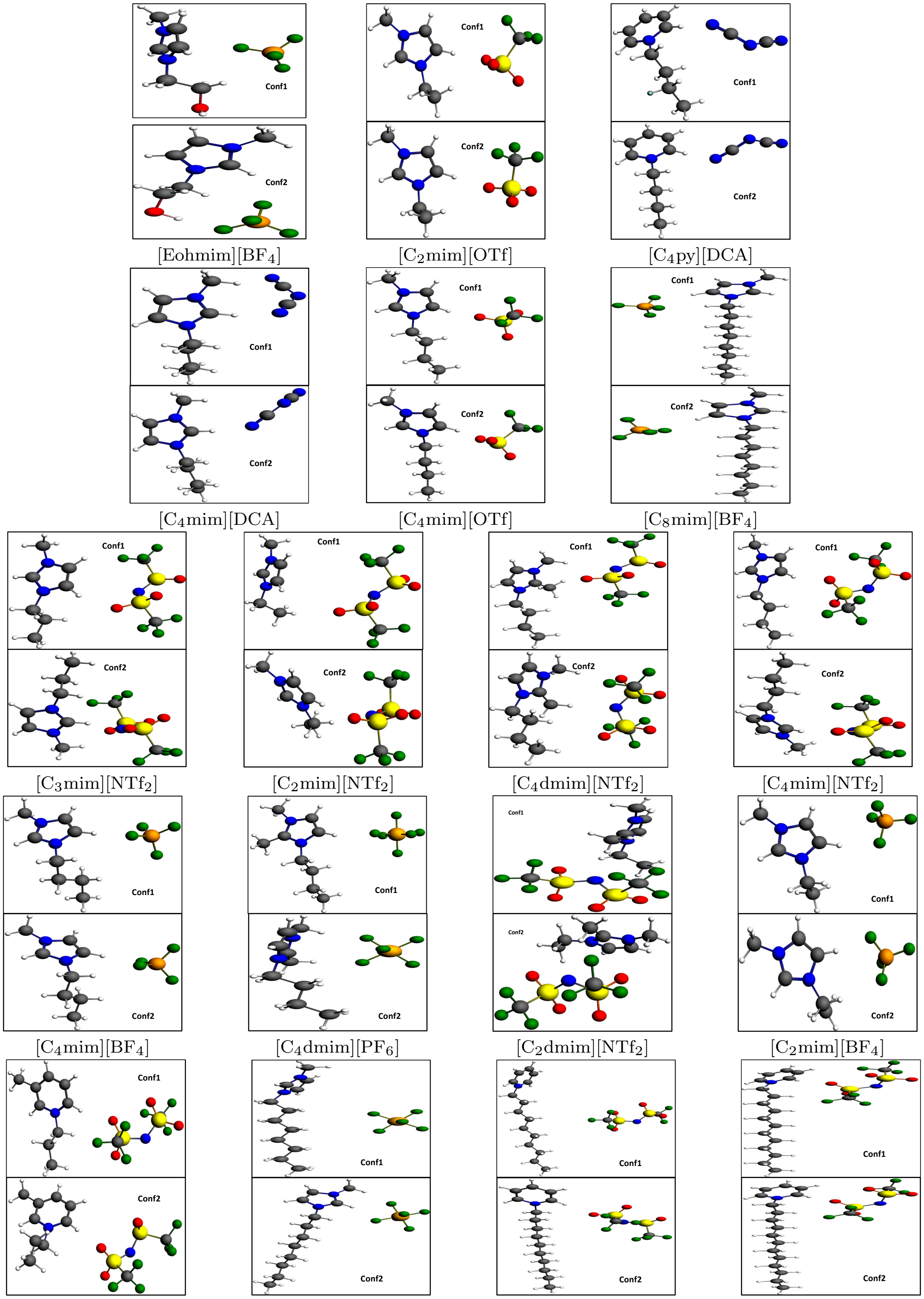


[C$_{10}$py][NTf2]



[C$_{12}$py][NTf2]

Figure. S 4: COSMO surface points of certain ionic liquids.



[Eohmim][BF$_4$] [C$_2$mim][OTf] [C$_4$py][DCA]

[C$_4$mim][DCA] [C$_4$mim][OTf] [C$_8$mim][BF$_4$]

[C$_3$mim][NTf$_2$] [C$_2$mim][NTf$_2$] [C$_4$dmim][NTf$_2$] [C$_4$mim][NTf$_2$]

[C$_4$mim][BF$_4$] [C$_4$dmim][PF$_6$] [C$_2$dmim][NTf$_2$] [C$_2$mim][BF$_4$]

[C$_3$mpy][NTf$_2$] [C$_8$mim][PF$_6$] [C$_{10}$py][NTf$_2$] [C$_{12}$py][NTf$_2$]

Figure. S 5: Two different conformers of 18 different ionic liquids.

Table S 2: The experimental and calculated solubility of CO_2 in 24 ionic liquids at 1 bar partial pressure and at ∼298 K.

Numbers	Ionic Liquids	Temperature (K)	Fugacity (bar)	Exp. H (bar)	Exp. Sol. (mol fraction)	COSMOSAC-LANL	COSMOSAC-2013
1	[C$_2$mim][BF$_4$]	298	64.09	81.06	0.012	0.010	0.016
2	[C$_4$py][DCA]	298.15	64.31	63.9	0.016	0.017	0.025
3	[C$_4$dmim][PF$_6$]	298.1	64.23	61.8	0.016	0.020	0.026
4	[C$_4$dmim][BF4]	298.1	64.23	61	0.016	0.017	0.026
5	[C$_4$py][F3Ac]	298.15	64.31	56.9	0.018	0.020	0.025
6	[C$_4$mim][BF$_4$]	298.1	64.23	56.5	0.018	0.014	0.021
7	[C$_4$mim][DCA]	298	64.09	55.9	0.018	0.019	0.028
8	[C$_4$mim][PF$_6$]	298.1	64.23	53.4	0.019	0.017	0.026
9	[C$_2$mim][OTf]	298.2	64.38	52	0.019	0.014	0.019
10	[C$_3$mim][PF$_6$]	298.1	64.23	52	0.019	0.013	0.018
11	[C$_4$mim][OTf]	298.15	64.31	45	0.022	0.020	0.025
12	[C$_2$dmim][NTf$_2$]	298.1	64.23	39.6	0.025	0.021	0.029
13	[C$_4$mpyr][NTf$_2$]	298.15	64.31	38.6	0.026	0.030	0.038
14	[C$_3$mim]NTf$_2$]	298.1	64.23	37	0.027	0.026	0.032
15	[C$_2$mim][NTf$_2$]	298.1	64.23	35.6	0.028	0.025	0.029
16	[C$_4$mim][NTf$_2$]	298.1	64.23	33	0.030	0.027	0.035
17	[C$_6$mpy][NTf$_2$]	298	64.09	32.8	0.030	0.030	0.039
18	[C$_4$py][NTf$_2$]	298.15	64.31	32	0.031	0.030	0.033
19	[C$_8$mim][NTf$_2$]	298.1	64.23	30	0.033	0.033	0.041
20	[C$_6$mim][NTf$_2$]	298.06	64.17	29.54	0.034	0.033	0.041
21	[C$_8$py][NTf$_2$]	298.15	64.31	27.9	0.036	0.032	0.043
22	[C$_{10}$py][NTf$_2$]	298.15	64.31	27.5	0.036	0.040	0.049
23	[C$_{12}$py][NTf$_2$]	298.15	64.31	27.1	0.037	0.040	0.051
24	[C$_8$h$_4$f$_{13}$][NTf$_2$]	298.04	64.14	25.3	0.040	0.032	0.040

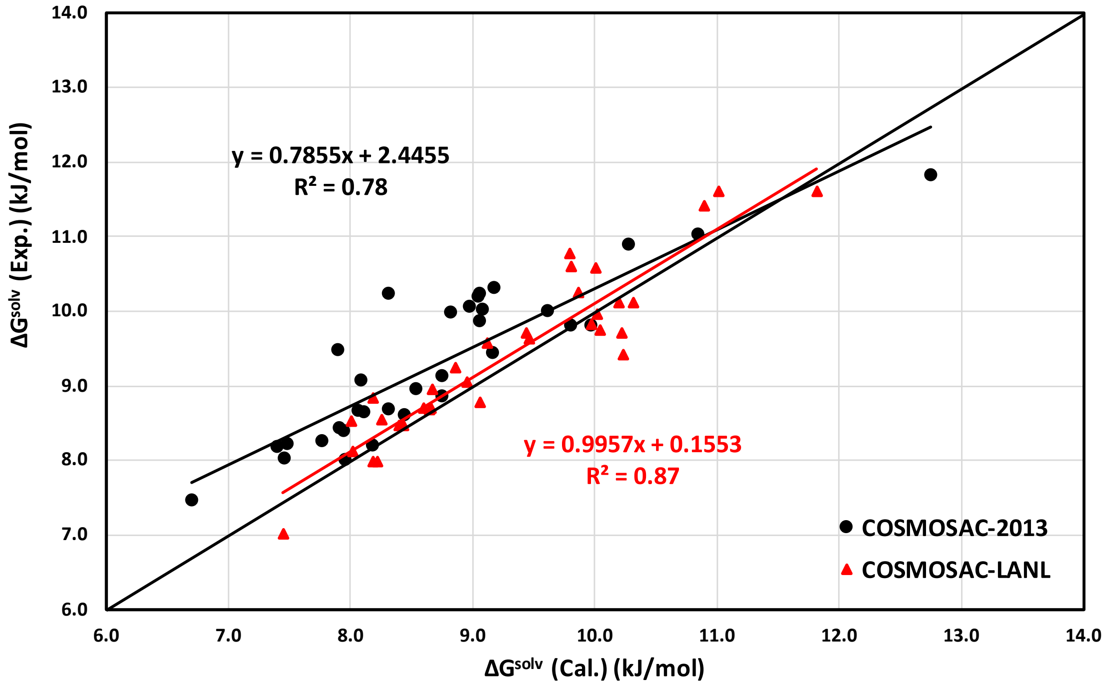


Figure. S 6: The calculated solvation free energy vs the experimental solvation free energy for 33 ionic liquids at room temperature and at 1 bar partial pressure.

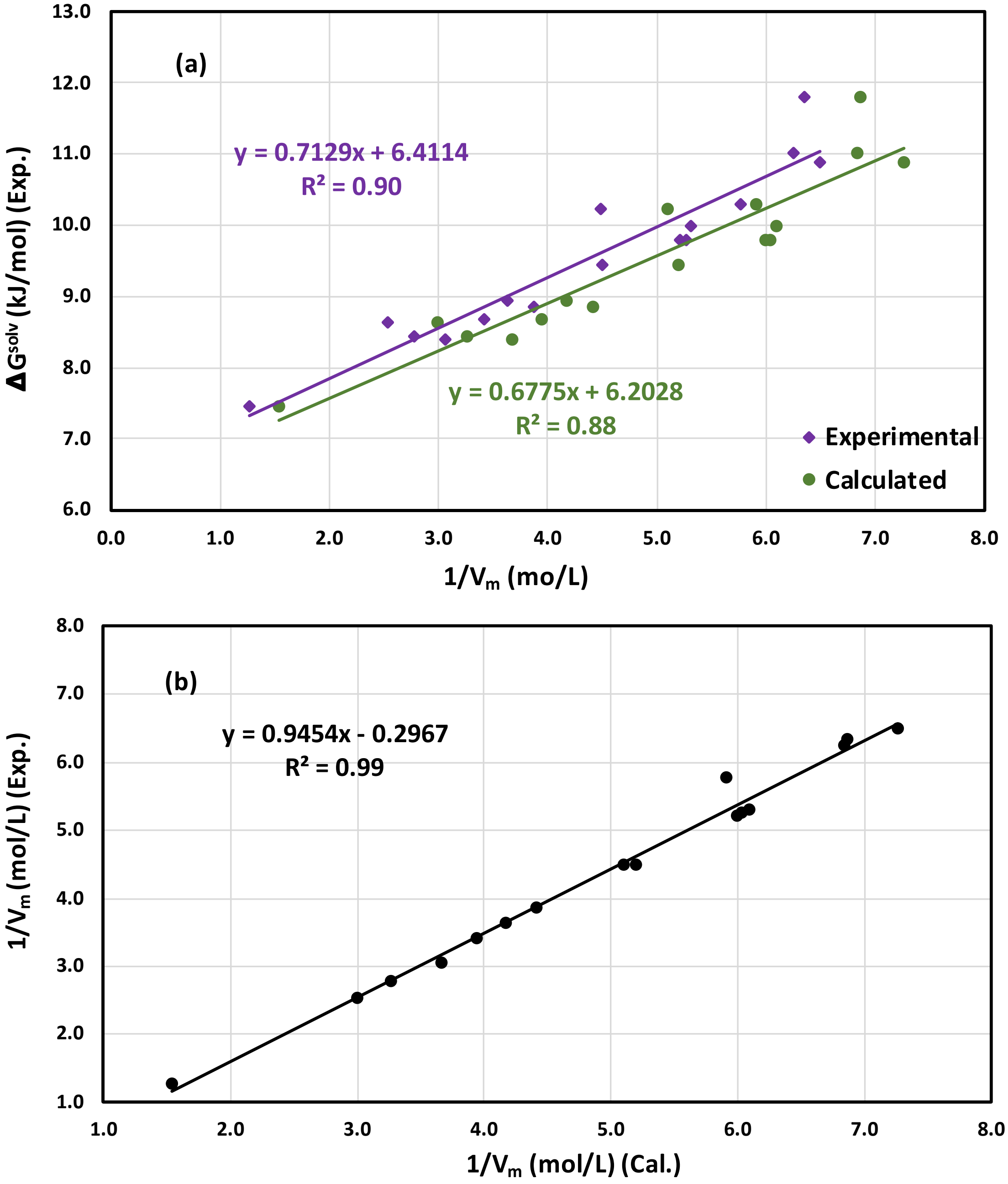


Figure. S 7: In fig.(a) the experimental ΔG^{solv} vs $1/V_m$ (exp) and ΔG^{solv} vs $1/V_m$ (cal) have been shown. In fig.(b) $1/V_m$ (exp) vs $1/V_m$ (cal) has been shown.

Table S 3: The experimental ΔG^{solv} (kJ/mol) and $1/V_m$ (mol/L) at 1 bar partial pressure

Ionic Liquids	Δ G^{solv}(kJ/mol)	V_m (Exp.)	$1/V_m$ (Exp.)	V_m (Cal.)	$1/V_m$ (Cal.)
[Eohmim][BF_4]	11.81	157.58	6.35	145.56	6.87
[C_2mim][BF_4]	10.89	154.03	6.49	137.77	7.26
[C_2mim][DCA]	11.01	159.93	6.25	146.26	6.84
[C_4py][DCA]	10.3	173.32	5.77	169.03	5.92
[C_4dmim][PF_6]	10.22	222.70	4.49	196.05	5.10
[C_2mim][OTf]	9.8	189.95	5.26	165.66	6.04
[C_3mim][PF_6]	9.79	191.60	5.22	166.89	5.99
[C_4mim][OTf]	9.44	222.45	4.50	192.29	5.20
[C_4mim][NTf_2]	8.67	292.85	3.41	253.68	3.94
[P_{66614}][eFAP]	7.45	786.52	1.27	651.98	1.53
[C_6mim][NTf_2]	8.39	326.34	3.06	272.53	3.67
[C_2mim][NTf_2]	8.85	258.45	3.87	226.65	4.41
[C_3mim]NTf_2]	8.95	274.80	3.64	239.61	4.17
[C_8mim][NTf_2]	8.43	360.50	2.77	306.44	3.26
[C_{10}mim][NTf_2]	8.64	393.99	2.54	333.64	3.00
[C_4mim][BF_4]	10.0	188.15	5.32	164.19	6.09

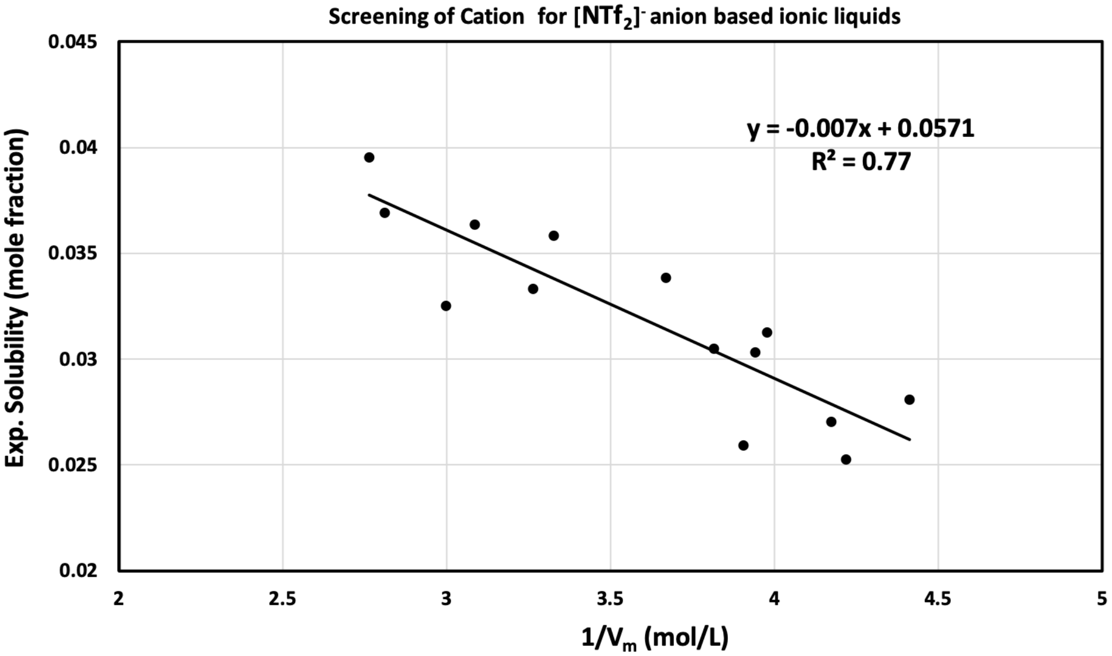


Figure. S 8: Relation between the experimental solubility and $1/V_m$ to screen the cation against $[NTf_2]^-$ anion.

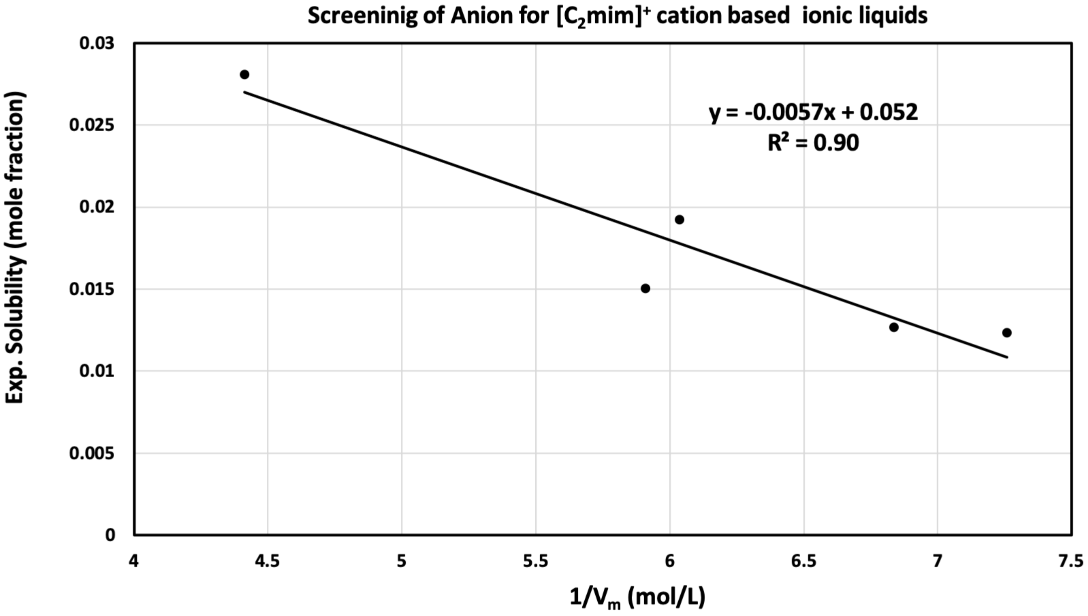


Figure. S 9: Relation between the experimental solubility and $1/V_m$ to screen the anion against $[C_2mim]^+$ cation.

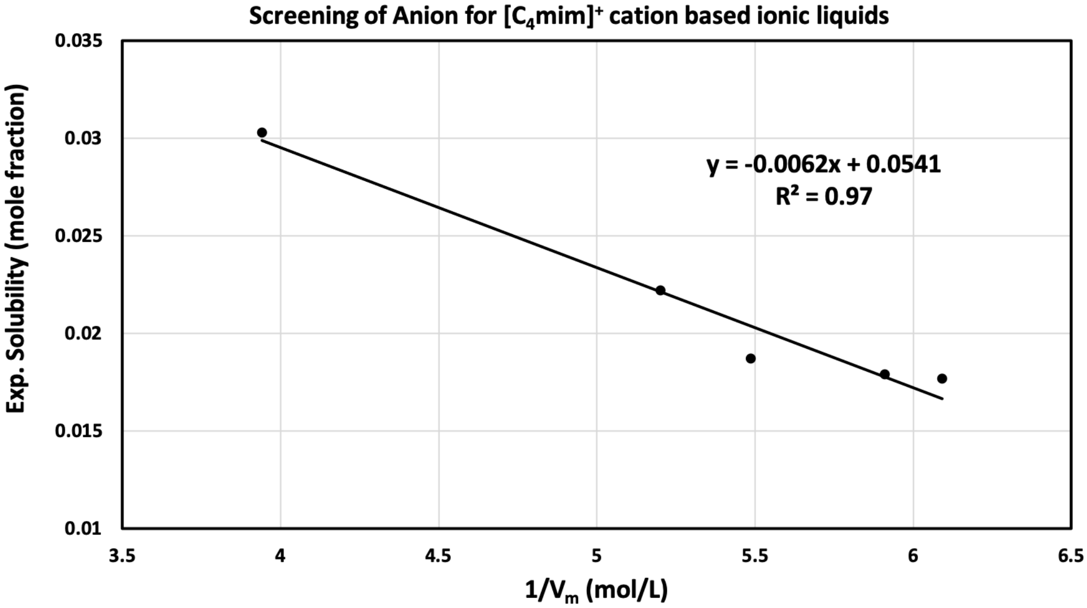


Figure. S 10: Relation between the experimental solubility and $1/V_m$ to screen the anion against $[C_4mim]^+$ cation.

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