

Predicting Sigma-Profile for Ionic Liquids Using COSMO

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Sigma profile/ COSMO/ Ionic liquid

ABSTRACT: Conductor-like screening models (COSMO) based on solvation thermodynamics and computational quantum mechanics have emerged with the aim of predicting mixture behavior supported on information of sigma profiles specific to each molecule only. A sigma profile is the probability distribution of a molecular surface segment which has a specific charge density. We describe the procedure for sigma profile generation using Materials Studio (MS) application, and we validate our database by comparing with literature. A python program and a procedure to generate additional sigma profiles is also provided. We display 24 sigma profiles which correspond with 24 different ionic liquids (IL). These IL share their anion, but their cation was rationally modified 24 times. Additionally, we use our determined sigma profiles to calculate the remaining net charge of those IL. Sensitivity analysis was performed to check the influence of every cation parameter on remaining net charge of IL, finding that number of hydrocarbon groups in the cation have the greatest impact.

Today, predictive models to calculate phase equilibrium of multicomponent systems and to account for liquid-phase nonidealities are gathering progressively more attention in process and product development. Solvation-thermodynamics methods come as a promising alternative in the aim of predicting molecular interactions and accounting for liquid-phase nonideality based on information of pure components only. Specifically, the COSMO-based models, which combine quantum chemical calculations with statistical thermodynamics, allow to estimate thermo-physical properties for species in a mixture without any experimental data [1].

COSMO-based models generate a surface-charge distribution which is used to compute probability distribution of a molecular surface segment with a specific charge density - named as sigma profile -. Conceptually, COSMO-based models place the molecule to be studied inside a cavity and into a conducting homogeneous solvent (Figure 1). The molecule's dipole and higher moments pull charges from the surrounding conductor medium to the surface of the cavity cancelling the electric field both tangential to the surface and inside the conductor. Finally, this surface-charge distribution is presented as a sigma profile [2].

The induced surface charges in a discretized space is determined by:

$$\Phi_{\text{tot}} = 0 = \Phi_{\text{sol}} + A \cdot q^*$$

Where:

Φ_{tot} : Total potential on the cavity surface.

Φ_{sol} : Potential due to the charge distribution of the solute molecule.

A: Coulomb interaction matrix. It describes potential interactions between surface charges and is a function of the cavity geometry.

q^* : Surface screening charge in the conductor.

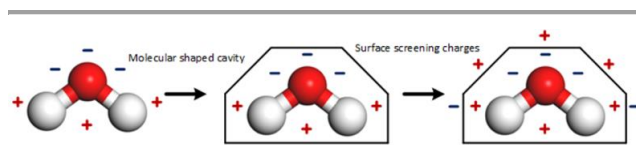


Figure 1. Ideal solvation process in the COSMO-based model: the molecule in the cavity within a perfect conductor. The molecule pulls charges from surrounding medium to the surface of the cavity.

The generated sigma profile is computed by a COSMO model - conductor-like screening models-realistic solvation (COSMO-RS) - to predict intermolecular interactions by using only molecular structure and a few adjustable parameters [2].

On the other hand, COSMO-SAC model - conductor-like screening models-segment activity coefficient - is a robust preliminary tool for fast screening and design of molecules to gas capture without relying on binary interaction parameters or experimental data. Two basic parameters: sigma profile (SGPRF1 - SGPRF5) and COSMO volume (CSACVL) are necessary to implement COSMO-SAC model in Aspen Plus. We provide that information for ionic liquids in this work [3, 4].

Therefore, COSMO-based model can be applied to generate sigma profiles for ionic liquids (ILs). ILs can be defined as a salt in the liquid state, and for an historical view, as salt with a melting temperature below the boiling point of water [5]. ILs are commonly composed of a bulky organic cation and either an organic or an inorganic anion. Their inherent polarity, high thermal stability, non-flammability, miscibility with organic compounds and non-volatility make them propitious for many engineering applications such as new solvents for chemical reactions [6], solvents for biopolymers [7], electrolytes for energy storage [8], electrochemical sensing [9] and environments for specific catalysis [10].

Results and discussion

Sigma profile

We generate 24 sigma profiles which correspond with 24 different ionic liquids. Chloride [Cl⁻] is maintained as the anion in every ionic liquid, but the cations were rationally modified 24 times (Figure 2). The COSMO calculations are performed separately from anion and cations using Materials Studio (MS) application. After import the selected molecule into MS, energy and geometry is optimized by fixing the atomic coordinates for the molecule and minimizing its total energy. The volume of the cavity around the molecule in the theoretical conducting medium and the condensed phase energy, the number of surface segments, and their charge is obtained from the COSMO calculations of every molecule (Supporting Information, Section A).

The COSMO calculation output, σ^* , is computed in our Python program to average the screening charge densities over a standardized bonding segment to determine a new surface-charge density, σ . This charge distribution is the probability distribution of a molecular surface segment which has a specific charge density – sigma profile, $p(\sigma)$. The sigma profile for a molecule i [11], $p_i(\sigma)$:

$$p_i(\sigma) = \frac{n_i(\sigma)}{n_i} = \frac{A_i(\sigma)}{A_i}$$

$$n_i = \sum_{\sigma} n_i(\sigma) = \frac{A_i}{a_{\text{eff}}}$$

$$A_i = \sum_{\sigma} A_i(\sigma)$$

Where:

σ : Discretized surface-charge density.

$n_i(\sigma)$: Number of segments with a discretized surface-charge density.

A_i : Total cavity surface area.

$A_i(\sigma)$: Total surface area of all the segments with a charge density σ .

a_{eff} : Effective surface area of a standard surface segment that represents the contact area between different molecules. Lin and Sandler [12] set a_{eff} to 7.5 Å.

The sigma profile of the mixture, cation and anion, is calculated as the weighted average of sigma profiles of pure components [13]:

$$p_s = \frac{\sum_i x_i \cdot n_i \cdot p_i(\sigma)}{\sum_i x_i \cdot n_i} = \frac{\sum_i x_i \cdot A_i \cdot p_i(\sigma)}{\sum_i x_i \cdot A_i}$$

The averaged surface-charge densities of ion i (σ_i) can be calculated using the following equation [11,12]:

$$\sigma_i = \frac{\sum_n \sigma_n^* \frac{r_n^2 r_{\text{av}}^2}{r_n^2 + r_{\text{av}}^2} \exp(-\frac{d_{\text{mn}}^2}{r_n^2 + r_{\text{av}}^2})}{\sum_n \frac{r_n^2 r_{\text{av}}^2}{r_n^2 + r_{\text{av}}^2} \exp(-\frac{d_{\text{mn}}^2}{r_n^2 + r_{\text{av}}^2})}$$

Where:

r_n : Radius of the actual surface segment (assuming circular segments).

r_{av} : Averaging radius (adjustable from 0.5 Å to 1 Å). We set averaging radius to be 0.5 Å, which is the best value reported by Klamt [14].

d_{mn} : Distance between two segments.

The calculated sigma profile of 1-butyl-3-methylimidazole chloride ([BMIM][Cl]) and that found in the literature [15] is shown in Figure 3. It serves as a visual tool to check the efficiency of our procedure and our Python code. The mismatch between sigma profile in literature and our pattern may come from our higher accuracy in energy and geometry optimization. The sigma profile of every ionic liquid can be determined by running the .txt document generated in MS program with our Python code.

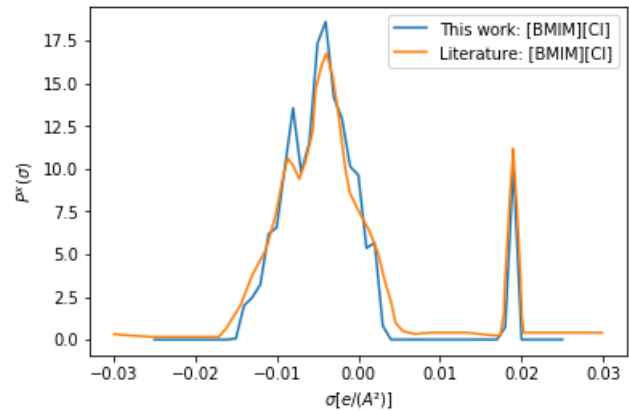


Figure 3. Sigma profiles of 1-butyl-3-methylimidazole chloride ([BMIM][Cl]) in literature and in this work.

Remaining net charge

The total charge of the IL after the contributions from cation and anion is named as remaining net charge of the IL. We use the generated sigma profiles to determine the remaining net charge of the ILs by using the following equation:

$$\text{Net Charge} = (-1) \cdot \frac{\sum_i n_i(\sigma) \cdot \sigma_i}{n}$$

Where:

σ_i : Discretized surface-charge density of a segment i .

n : Total number of segments.

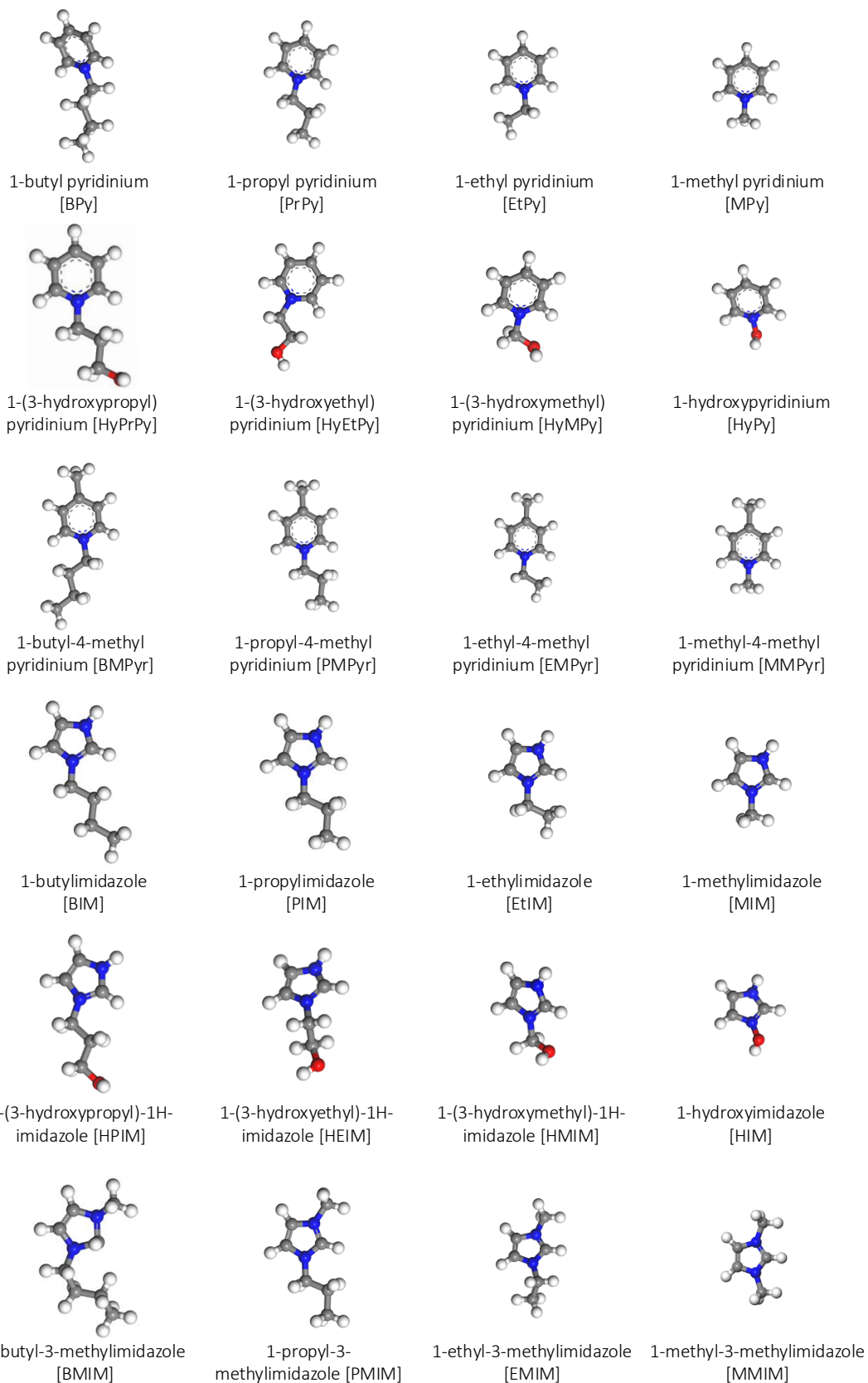


Figure 2. List of cations employed in this investigation.

We analyze and determine the remaining net charge of 24 sigma profiles which correspond with 24 different ILs. The cations are rationally modified 24 times and the anion, which is chloride [Cl], is maintained. It is systematically added one hydrocarbon in the 1-position into the pyridinium cycle of the cations, thus getting 1-butyl pyridinium [BPy], 1-propyl pyridinium [PrPy], 1-ethyl pyridinium [EtPy] and 1-methyl pyridinium [MPy]. Not only the remaining net charge of their corresponding ILs ([BPy][Cl], [PrPy][Cl], [EtPy][Cl] and [MPy][Cl]) (Table 1), but also the net charge tendency as a function of hydrocarbon group length is calculated (Figure 4). The net charge tendency is ascribed to a second-order polynomial regression (Table 2).

Ion liquid	Net charge	Ion liquid	Net charge	Ion liquid	Net charge
[BPy][Cl]	0.00347	[HyPrPy][Cl]	0.00354	[BMPyr][Cl]	0.00330
[PrPy][Cl]	0.00364	[HyEtPy][Cl]	0.00371	[PMPyr][Cl]	0.00347
[EtPy][Cl]	0.00387	[HyMPy][Cl]	0.00382	[EMPyr][Cl]	0.00364
[MPy][Cl]	0.00387	[HyPy][Cl]	0.00388	[MMPyr][Cl]	0.00376
Ion liquid	Net charge	Ion liquid	Net charge	Ion liquid	Net charge
[BIM][Cl]	0.00360	[HPIM][Cl]	0.00367	[BMIM][Cl]	0.00341
[PIM][Cl]	0.00376	[HEIM][Cl]	0.00379	[PMIM][Cl]	0.00358
[EIM][Cl]	0.00387	[HMIM][Cl]	0.00388	[EMIM][Cl]	0.00373
[MIM][Cl]	0.00389	[HIM][Cl]	0.00385	[MMIM][Cl]	0.00385

Table 1. Net charge of the 24 ILs.

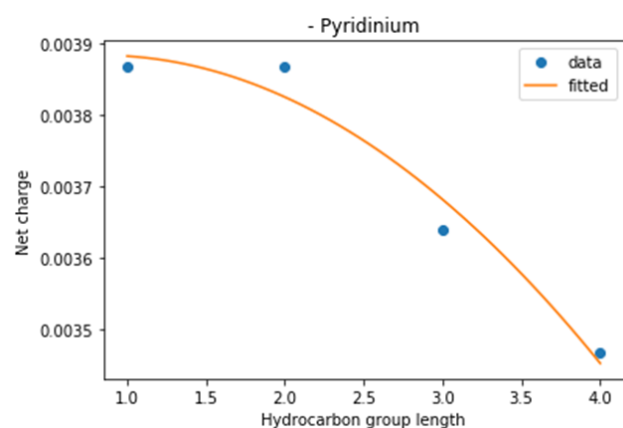


Figure 4. Net charge as a function of hydrocarbon group length in pyridinium cycle.

	a	1 st. der.	b	1 st. der.	c	1 st. der.
Regr. I. Pyridinium cycle alone	-4.31E-05	3.21E-05	7.19E-05	1.63E-04	3.85E-03	1.79E-04
Regr. II. Pyridinium cycle functionalized with hydroxy group	-2.93E-05	3.19E-06	-2.63E-05	9.98E-06	3.88E-03	6.21E-06
Regr. III. Pyridinium cycle functionalized with methyl group	-1.34E-05	5.17E-06	-8.81E-05	2.63E-05	3.86E-03	2.88E-05
Regr. IV. Imidazole cycle alone	-3.37E-05	6.76E-06	7.24E-05	3.43E-05	3.85E-03	3.76E-05

Regr. V. Imidazole cycle functionalized with hydroxy group	-3.79E-05	9.20E-06	5.20E-05	2.88E-05	3.85E-03	1.79E-05
Regr. VI. Imidazole cycle functionalized with methyl group	-1.37E-05	4.14E-07	-7.63E-05	2.10E-06	3.94E-03	2.31E-06

Table 2. Second order polynomial regression results.

Moreover, hydroxy and methyl functional groups are, separately, introduced into the pyridinium cycle at the end of the hydrocarbon group and in para position, respectively. Therefore, the remaining net charge of 1-(3-hydroxypropyl) pyridinium chloride [HyPrPy][Cl], 1-(3-hydroxyethyl) pyridinium chloride [HyEtPy][Cl], 1-(3-hydroxymethyl) pyridinium chloride [HyMPy][Cl], 1-hydroxypyridinium chloride [HyMPy][Cl], 1-butyl-4-methyl pyridinium chloride [BMPyr][Cl], 1-propyl-4-methyl pyridinium chloride [PMPyr][Cl], 1-ethyl-4-methyl pyridinium chloride [EMPyr][Cl] and 1-methyl-4-methyl pyridinium chloride [MMPyr][Cl] is calculated (Table 1). It is also determined the net charge tendency as a function of hydrocarbon group length when those functional group are introduced (Figure 5). Their net charge tendencies are also ascribed to a second order polynomial regression (Table 2).

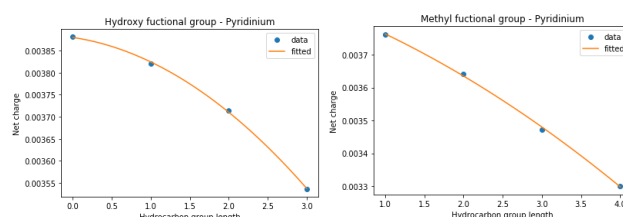


Figure 5. a) Net charge as a function of hydrocarbon group length in pyridinium cycle functionalized with the hydroxy group. b) Net charge as a function of hydrocarbon group length in pyridinium cycle functionalized with the methyl group.

Furthermore, we change the cycle group to imidazole and perform a similar analysis. We systematically added one hydrocarbon in the 1-position into the imidazole cycle of the cations, thus getting 1-butylimidazole chloride [BIM][Cl], 1-propylimidazole chloride [PIM][Cl], 1-ethylimidazole chloride [EIM][Cl] and 1-methylimidazole chloride [MIM][Cl] ILs. In addition, hydroxy and methyl functional groups are, separately, introduced into the imidazole cycle at the end of the hydrocarbon group and in 3-position, respectively, thus getting 1-(3-hydroxypropyl)-1H-imidazole chloride [HPIM][Cl], 1-(3-hydroxyethyl)-1H-imidazole chloride [HEIM][Cl], 1-(3-hydroxymethyl)-1H-imidazole chloride [HMIM][Cl], 1-hydroxyimidazole chloride [HPIM][Cl], 1-butyl-3-methylimidazole chloride [BMIM][Cl], 1-propyl-3-methylimidazole chloride [PMIM][Cl], 1-ethyl-3-methylimidazole chloride [EMIM][Cl] and 1-methyl-3-methylimidazole chloride [MMIM][Cl] ILs. As for pyridinium cycle base-cations, it is determined the net charge tendency as a function of hydrocarbon group length with and without introducing functional group (Table 1). Their net charge tendencies are also ascribed to a second order polynomial regression (Figure 6, Table 2).

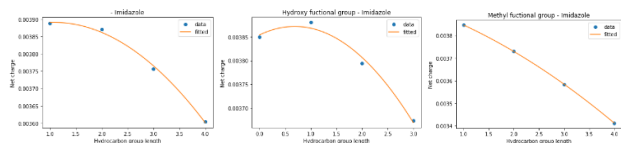


Figure 6. a) Net charge as a function of hydrocarbon group length in imidazole cycle. b) Net charge as a function of hydrocarbon group length in imidazole cycle functionalized with the hydroxy group. c) Net charge as a function of hydrocarbon group length in imidazole cycle functionalized with the methyl group.

Sensitivity analysis

We create a model that allow to determine the net charge of any created ILs as a function of the kind of cycle, the presence of hydroxy and/or methyl functionalization and the length of the hydrocarbon group:

$$\text{Net Charge} = \{(1 - \text{Kind}_{\text{cycle}}) \cdot [(1 - \text{OH}_{\text{presence}} - \text{Methyl}_{\text{presence}}) \cdot \text{Regression}_I + \text{OH}_{\text{presence}} \cdot \text{Regression}_{II} + \text{Methyl}_{\text{presence}} \cdot \text{Regression}_{III}] + \{\text{Kind}_{\text{cycle}} \cdot [(1 - \text{OH}_{\text{presence}} - \text{Methyl}_{\text{presence}}) \cdot \text{Regression}_{IV} + \text{OH}_{\text{presence}} \cdot \text{Regression}_V + \text{Methyl}_{\text{presence}} \cdot \text{Regression}_{VI}]\}$$

Where:

$\text{Kind}_{\text{cycle}}$: Kind of cycle:

0 = pyridinium cycle.

1 = imidazole cycle.

$\text{OH}_{\text{presence}}$: Hydroxy functionalization:

0 = No functionalization.

1 = Functionalization.

$\text{Methyl}_{\text{presence}}$: Methyl functionalization:

0 = No functionalization.

1 = Functionalization.

Sensitivity analysis is realized to validate the model. Global sensitivity analysis is performed using Morris Method. The results of this analysis are presented in Figure 7. As can be seen, the hydrocarbon group length is the most important parameter in the final net charge of the ILs, followed by the methyl functionalization, the hydroxy functionalization and, finally, the kind of cycle. Additionally, all four model parameters influence the net charge on the same order of magnitude, indicating that there are no low-impact parameters that should be removed from the model. Furthermore, the net charge for 3,000 networks computed in the sensitivity analysis was plotted individually with respect to each of the four texted model parameters (Figure 8).

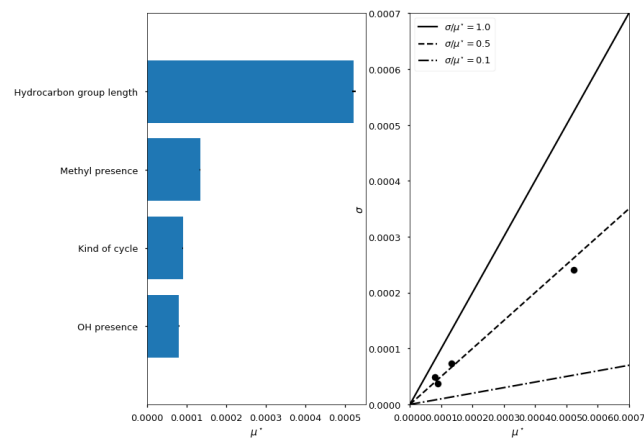


Figure 7. Sensitivity analysis results showing the relative sensitivity of the net charge of the ILs to the four texted parameters.

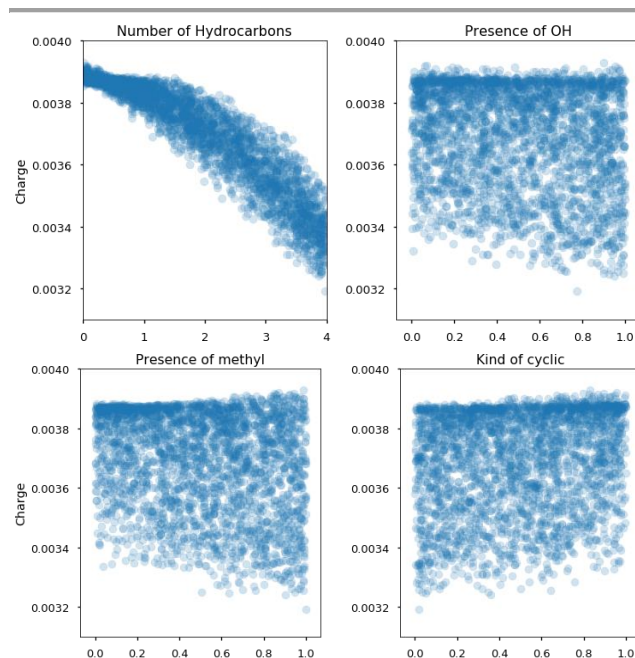


Figure 8. Scatter plots showing net charge individually with respect to each of the four tested model parameters.

Conclusions

Materials Studio application was employed to generate 24 sigma profiles which correspond with 24 different ionic liquids by using solvation thermodynamics and computational quantum mechanics - conductor-like screening models (COSMO) -. It was provided a python program and a procedure to generate additional sigma profiles. The remaining net charge of those ionic liquids was obtained by employing our calculated sigma profiles. The influence of every cation parameter on remaining net charge of the ionic liquids was determined with sensitivity analysis, finding that the number of hydrocarbon groups in the cation has the greatest impact.

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