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Multivariate Statistical Evaluation of Ionic Liquids Features for CO₂ Capture

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Abstract

The main goal of this work is to verify the possibility of the improving the process variables in CO₂ capture process using ionic liquids as sorbent, by changing the anions and/or cation type of the Ionic liquids. ANOVA models a PCA were performed for CO₂ capture capacity, viscosity, melting degradation temperature and chemical information of the ionic liquids. The results shows that tuning of ionic liquids are statistically significant and the resultants insights could be used to predict new sorbents.

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Keywords: Carbon capture; Ionic liquids; Multivariate analysis

1. Introduction

Several compounds that are classified as Ionic Liquids (IL) are known by its capacity to solubilize sour gases, mainly carbon dioxide [2]. Nowadays IL are established as the main alternative to amine technology for CO₂ separation [2]. Despite the lesser ILs CO₂ sorption capacity when compared to amines, the latter consume significant amount of power in the regeneration step, present high vapor pressure and are promptly degraded by heat [3]. In the search for new IL all these properties must be accounted, as well as the sorbent melting point in the case

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of pure ILs. The ILs are molten salts based on inorganic and organic asymmetrical cations and anions, and due to the possibilities of cation and anion combinations, the number of possible IL scale to 10^{19} [4]. The ILs physicochemical properties are said to be tunable by the changing of cation and anions, hence the desirable properties could be achieved knowing how they are influenced by these changes. The IL that are designed for specific applications is commonly referred as Task Specific Ionic Liquids (ref), and due to the number of synthesis possibilities the selecting process and property tuning are said to be impractical by experimental means [1]. Multivariate statistical approaches are useful to provide screening and optimization of several variables at same time [5], and was used in this study to evaluate information retrieved from the literature for 29 ILs, combinations of 6 different anions and 6 different cations. Among that information were the properties of interest for carbon dioxide capture processes, which are called response variables: CO₂ Henry constants, degradation temperatures (DT), melting points (MP) and viscosities. Other proprieties are chosen to be only explanatory variables that are called covariates: density, molecular weight, ramifications length, and molecular volume. The aim of this work was to verify the possibility of tuning the response variables through changing the cation and anions by means of ANOVA models, testing the significance of the effects of its composition for the four response variables cited. In addition to this goal, were tested whether relationships between covariates and the desirable properties could be created or not. This was done using Principal Component Analysis as multivariate data exploration tool to provide visualization of the underlying data structure to all variables simultaneously.

2. Material and Methods

Analysis of Variance (ANOVA) was employed to verify the statistical significance of the relationship between the cation and anion types with the response variables, by means of comparing the variances and applying the F-test. Principal component Analysis (PCA) was employed to evaluate the dependence of the response variables with each other and with the covariates, also to capture underlying patterns such as groupings. PCA works creating new variables, known as principal component (PC), through an algorithm that make linear combinations of the original variables, the PCs contains the data's set variance direction indicating the principles variables and patterns.

For the ANOVA models were retrieved data of 22 IL from literature, which were classified in groups respecting to their cations and anions. Due to the frequency of imidazolium cations, they were divided in three groups: MIa being for those cations with three or less carbons in the longest side chain; MIb being for those cations with five or more carbons in the longest side chain; and a group only for 1-methyl-3-butylimidazolium cation (C4MI). Other cation type used was pyridinium cations, including 4-methyl-N-butylpyridinium, N-butylpyridinium and N-butyl-N-methylpyridinium, which were represented as a single group named "py". The anion group also has four treatments, in respect to the following anions: tetrafluorophosphate borate, chloride, bis fluoromethyl sulfonyl imides and hexafluorophosphate. The relationships between the response variables and the types of cation and anions were tested through the ANOVA models for 95% of confidence interval. The response variables considered were Henry Constant (HC), Degradation Temperature (DT), Melting Point (MP) and IL dynamic viscosities.

The PCA was applied in numeric matrix with twenty lines (objects) and eight columns (variables), with centering in the average mean and scaling with standard deviation, allowing the analysis of variables with different scales, units and ranges. The variables were composed by the four response variables that were used in ANOVA and other four variables: density, molecular weight, ramifications length, and molecular volume. Seven ILs used in PCA are not used in ANOVA, and nine used in ANOVA are not used in PCA, by the data availability. The new IL included counted with N(CN₂) (dyacyaonoamides) and Tfo (trifluoromethylsulfonate) anions, also quaternary ammonium cations.

The IL data were retrieve from a dataset of all IL information available in open access works [6], with exception of carbon dioxide solubility data (HC) that are from [7]

3. Results and Discussion

The ANOVA results in the confirmation of the possibilities of tuning CO₂ Henry constants, viscosities and degradation temperatures. There is no significant statistical correlation for MP. In the Table 1 shows the results for ANOVA model for the hypothesis of relationship between HC values and the anion and cation types. The effects of

both treatments are shown as statistical significant by the p -value <0.05 . Comparing the mean squares values is possible to say that the anion type effect has more importance than the cation for determining the IL HC values. The pyridinium treatment is the cation with less data mean deviation and HC mean value, hence, showing as the cation with the best solubility performance (Figure 1). In the anion's context, both TFSI and Cl show the lesser HC values, the TFSI has the lesser mean value and large sample size.

Table 1: ANOVA model results for HC dependency with the IL cation and anion type

	DF	Sum of Squares	Mean Square	F-value	P-value
Anion	3	881.3	293.78	8.526	0.00265
Cation	3	750.7	250.25	7.262	0.00491
Residuals	12	413.5	34.46		

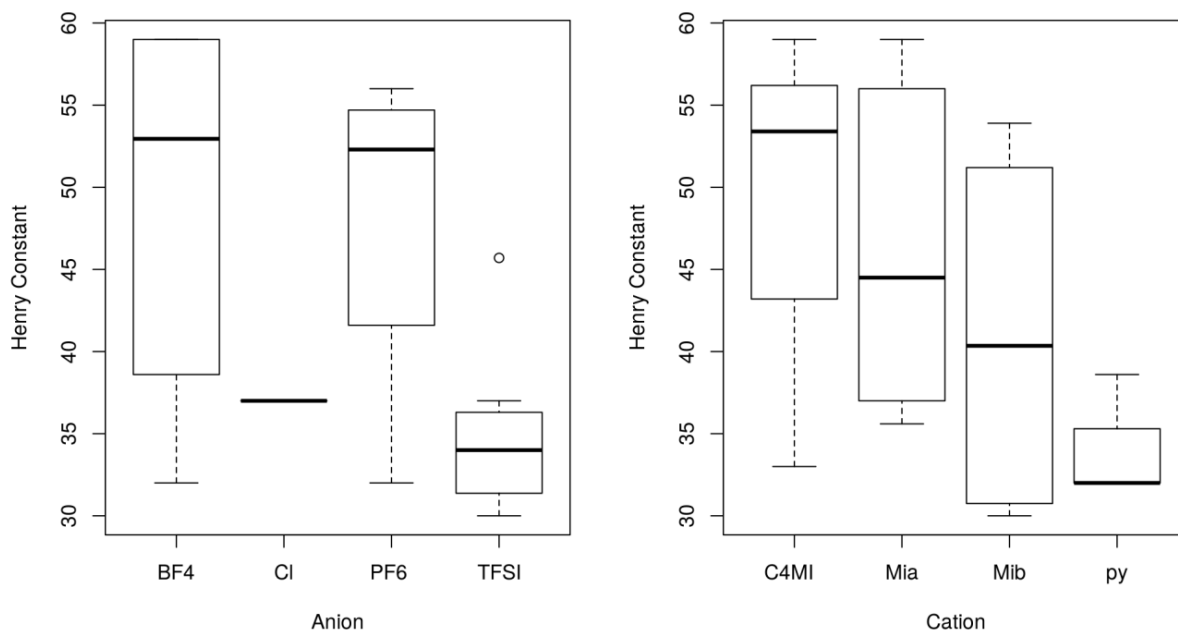


Figure 1: Distribution of HC values for each Anion and Cation

The ANOVA results for DT relationships for cation and anion types are in Table 2. The Anion types have significant greater effect than cation for the variation of the DT values, which also have a no neglected effect in it. In the Figure 2 is possible to observe that the IL that have TFSI anions correspond to the highest DT mean value. The IL with Chloride anions correlate with very low values of DT that are analysed. For the cations type the DT values are more dispersed, with overlaps between the treatments distributions, which may be the cause of its less effect importance.

The cation type that show higher thermic stability was the imidazolium cations with three or less carbons in the main side chain. Pyridinium cations also shows relatively DT values with low deviation, and for the others two types of cations accounted.

Table 2: ANOVA results for DT in function to cation and anion

	Degrees of Freedom	Sum of Squares	Mean Square	F value	P-value
Anion	3	72955	24318	70.28	1.45e-06
Cation	3	11638	3879	11.21	0.00215
Residuals	9	3114	346		

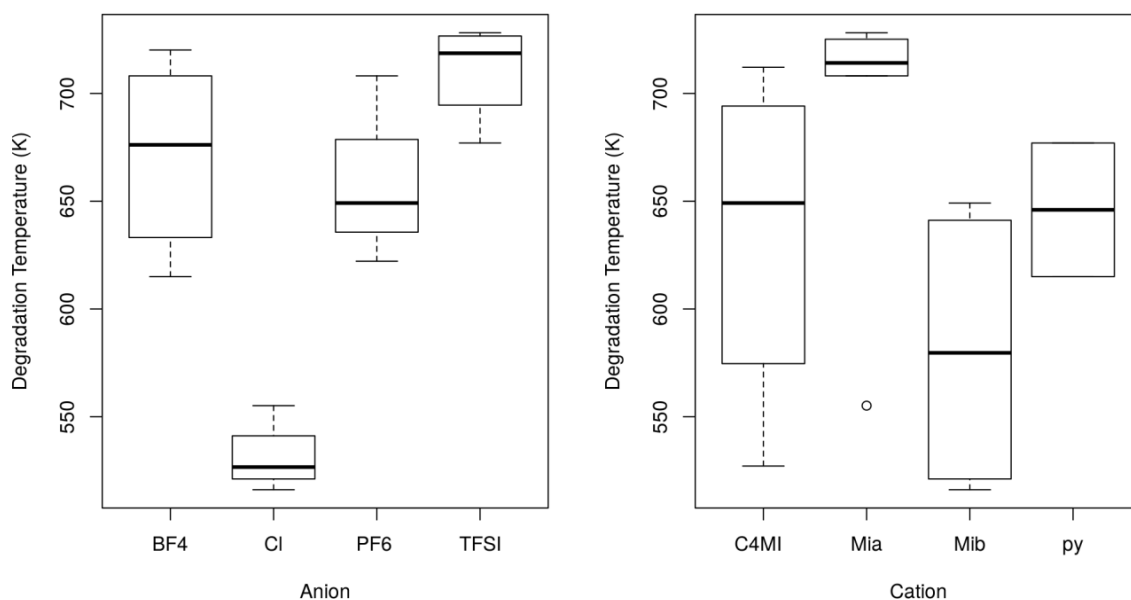


Figure 2: Distribution of the DT values in function of Anion and Cation

The first ANOVA model for MP relationship to the cation and anion was non-significant, mainly for anion, because that in the second model was only considered the cation type (Table 3). Even though, the p-value is greater than 0.5 and 0.1, showing they are not possible to discard the null hypothesis even for 90% interval of confidence. Although, the cations conserve some important variance and could be used in another models to try to predict MP. In Figure 3 are shown the distribution of MP values in function of cation and anion type. For cation type, the imidazolium cations with the main side chain greater than four have the lesser values of melting point. The pyridinium cation has the highest mean values of MP but not the highest possible values that are presented by the others two cations.

Table 3: Anova results for MP in function of Cation Type

	Degrees of Freedom	Sum of Squares	Mean Square	F value	P-value
Cation	3	11361	3787	1.725	0.215
Residuals	12	26346	2195		

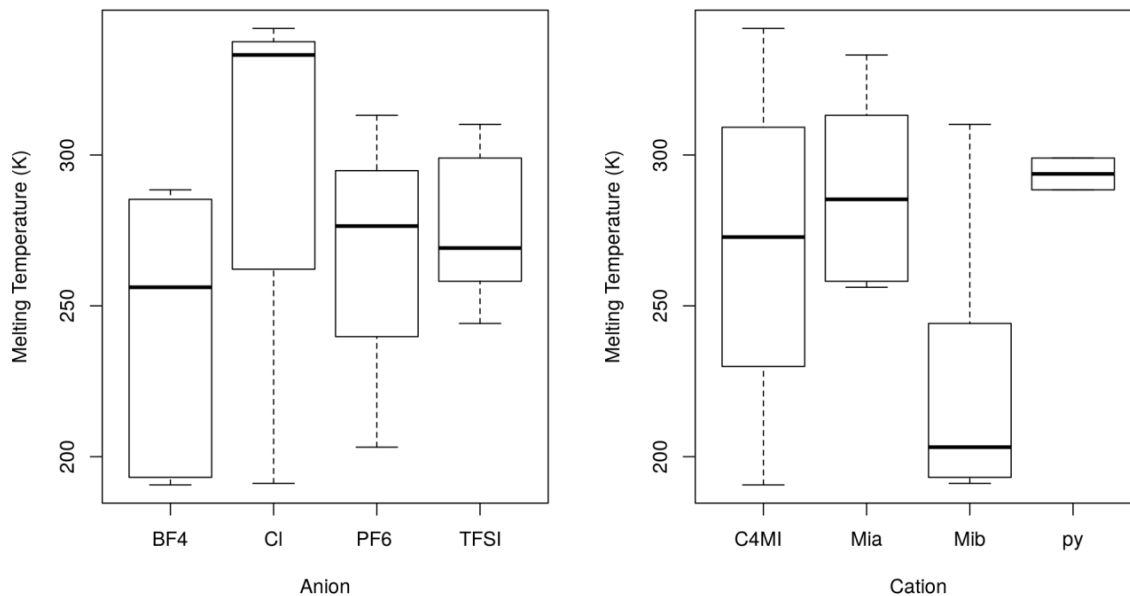


Figure 3: Distribution of the MP values in function of Anion and Cation.

The viscosity ANOVA models results for its relationship with cations and anion types are shown in the Table 4, with the two variables presenting significant effects. The anion type is dominant effect for the viscosity values for the IL tested. The IL composed with TFSI anion showed the lesser viscosity values with low dispersability, the same behaviour was found for IL that have pyridinium cations as showed in Figure 4.

Table 4: Anova results for Viscosity in function of Cation and Anion type

	Degrees of Freedom	Sum of Squares	Mean Square	F value	P-value
Cation	3	216893	72298	5.047	0.02202
Anion	3	438149	146050	10.195	0.00219
Residuals	10	143256	14326		

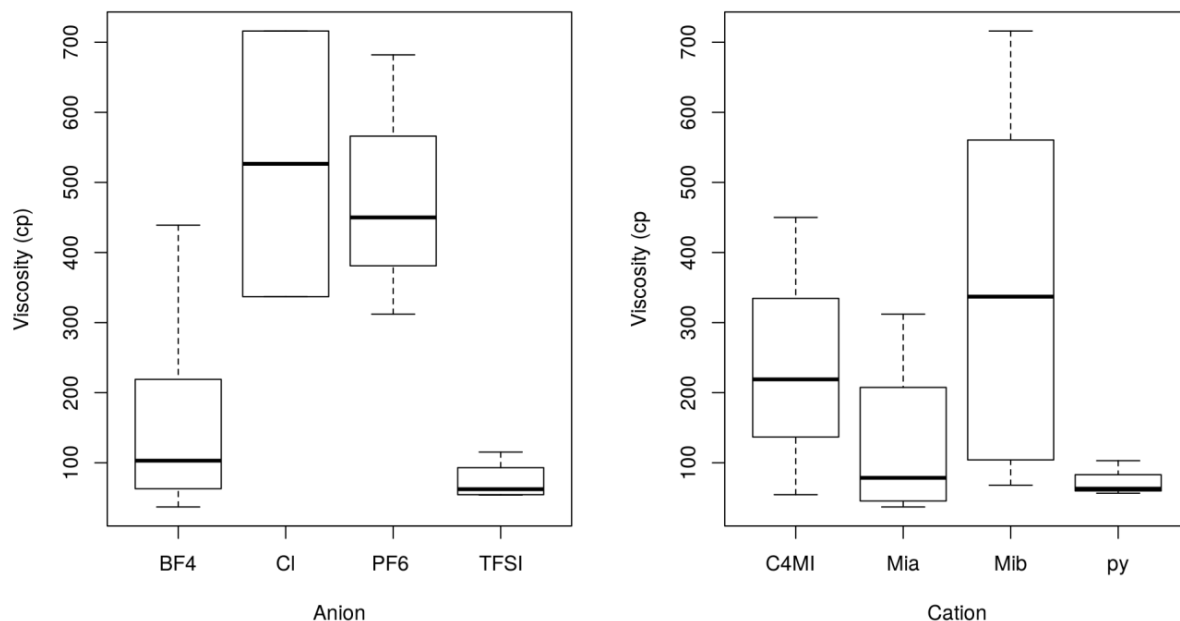


Figure 4: Distribution of the viscosity values in function of Anion and Cation.

The PCA resulted in seven principal components (PCs), with the two first summarizing 77% of the cumulative variance (Table 5). The PCA provides a satisfactory dimensionality reduction with two first PCs that were used to graphically represent the underlying patterns for the eight analysed variables. In Table 6 the loadings for the original variables are showed representing its contribution in each PCs, i.e., to that variance source. The similarity in the sign and magnitude of loadings values indicate correlation between that variables, and the contrary also is true. The HC variable shows a significant negative correlation with molar volume and molar mass in the most important data source of variance (PC1). In the PC2, that represents 30% of the data variation, the MP shows negative correlations with the carbon length in the main chain and the viscosity. The correlations in the others PCs are not so significant as the others. This correlations are plotted in the Figure 5 as the red arrows with represent the loadings directions and magnitudes. The dots are the PCA scores for the original objects values in the variables that make the plotted PCs. One important property of the scores are that their similarity of values in the most important PCs also represent the similarity in the characteristics expressed by the analysed variables. In Figure 6 the proximity of the points in the two firsts PCs trying to observe groupings in ILs in function of anion type and whether particularity of its properties will remain in th PCA transformed space. The IL with TFSI anion presenting high similarity, BF4 anions also maintain a grouping pattern mainly because the points similarity values in PC1 that holds 50% of the explained variance. The proximity in the PC1 also is observed for PF6, but with large difference in PC2. For the cation type, in Figure 7, the groups are more sparsed horizontally parallel to the PC1 axis, which indicate that the variance due to cation type is more correlated with PC2, and have less importance than the anion type. The ILs that have ammonium cations forms the group with more similarity than the others cation types groups.

Table 5: Summary data for the resulted PCs

	PC1	PC2	PC3	PC4	PC5	PC6	PC7
Standard deviation	1.8034	1.4668	0.8904	0.69539	0.54318	0.15559	0.02171
Proportion of Variance	0.4646	0.3074	0.1133	0.06908	0.04215	0.00346	0.00007
Cumulative Proportion	0.4646	0.7720	0.8852	0.95432	0.99647	0.99993	1.00000

Table 6: Loadings values for the original variables for each PC

	PC1	PC2	PC3	PC4	PC5	PC6	PC7
Molecular Mass (MM)	0.537	0	-0.134	-0.163	0.314	-0.213	0.722
Number of carbons in side chain (nCL)	0.257	-0.545	0.405	0	-0.129	0.668	0
Molecular Volume	0.508	-0.197	0	-0.270	0.342	-0.259	-0.663
Density	0.375	0.304	-0.604	0.306	0	0.524	-0.172
Viscosity	0	-0.574	-0.177	0.737	0	-0.307	0
MP	0.151	0.459	0.632	0.503	0.338	0	0
HC	-0.473	-0.169	-0.129	0	0.806	0.268	0

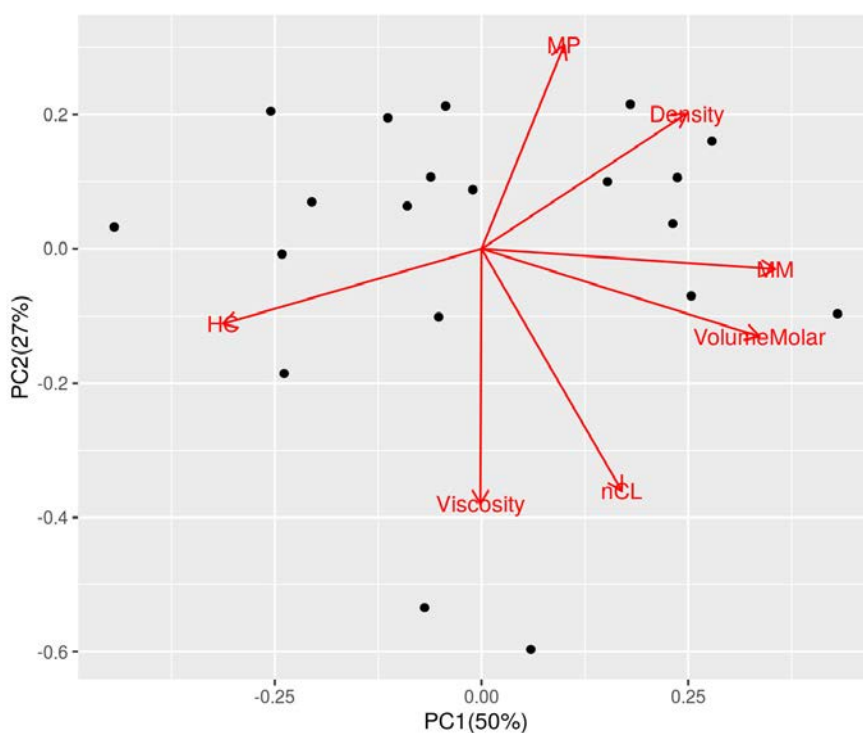


Figure 5: PCA plot of loadings and scores simultaneously, for PC1 and PC2

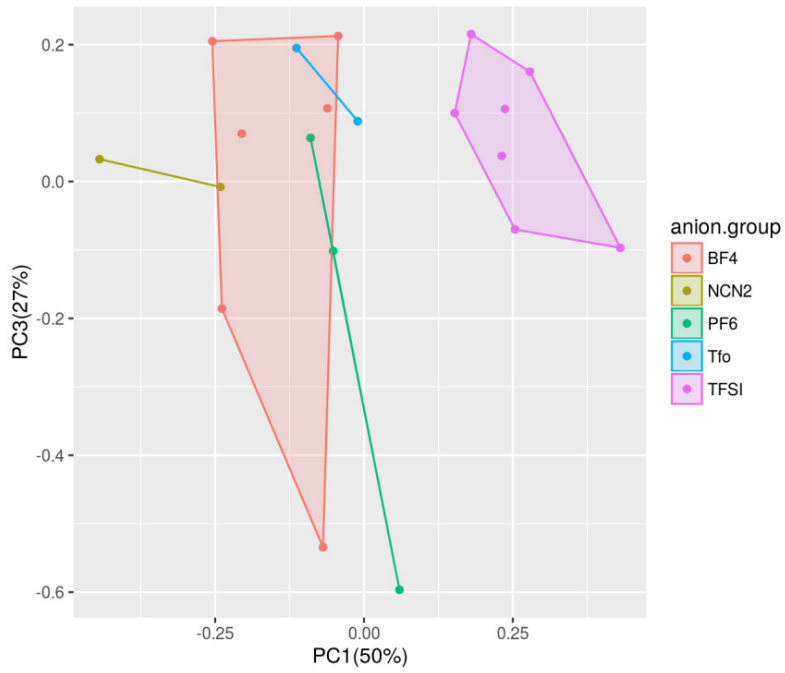


Figure 6: PCA scores plot with clustering in function of the anion type

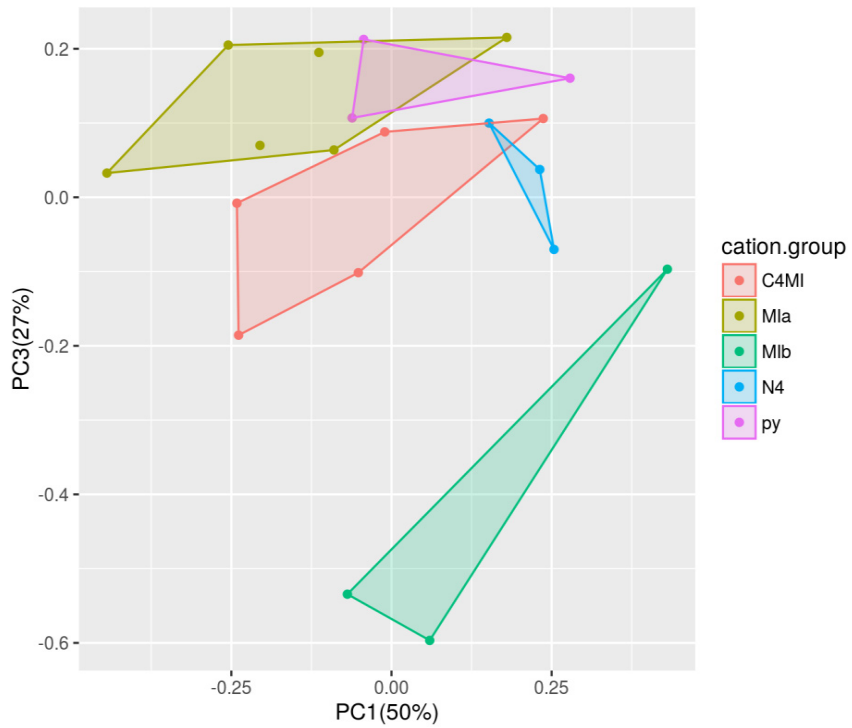


Figure 7: PCA scores plot with clustering in function of the cation type

Bringing together the ANOVA and PCA results for these IL, the general trend for the properties studied is that the anion type is responsible for the dominant effect. The cation type also presented a role, but with less intensity. The ILs with TSFI anion shows the better performance in the CO₂ sorption capacity, minor values of viscosity, high thermic resistance and with MP beneath the process temperature. Also, these ILs form a very similar group for the response variables and the covariates, which points to the dominant character of this anion type. The ILs with pyridinium cation type shows the best performance in CO₂ sorption and does not have the worst values for the others response variables. The HC values does not present correlation with viscosity and MP, and tends to be smaller in ILs that have high values of molecular mass and molecular volume, i.e., the carbon dioxide solubility is greater in bigger and multi atomic ions, which corroborate in some way with the Free Volume hypothesis. The melting point is tends to be higher in more viscous IL, and that have smaller side chains, although this pattern is not dominant and only indicate that smaller side chain could improve in these two process variables.

4. Conclusions

The tuning ability by changing the cation and anion type for improving the CO₂ capture process was confirmed with statistical significance for the IL studied in this work. We conclude that multivariate analysis approaches and techniques are useful for explore such multifactorial substances in complex process. The best IL that could be predicted by ANOVA and PCA results would be a combination of a pyridinium cation and a TFSI anion, with short side chain for smaller melting point values and large side chains for smaller Henry constants.

Acknowledgements

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