COMPUTER-AIDED MOLECULAR DESIGN FOR VISCOSITIES AND MELTING POINTS OF IONIC LIQUIDS

Hiroshi Yamamoto[1], *Tomohiko Okamura*[2], *Hiroyuki Matsuda*[2], *Kiyofumi Kurihara*[2], *and Katsumi Tochigi*[2]

[1] Asahi Glass Co. Ltd., Yokohama, Japan

[2] Department of Materials and Applied Chemistry, Nihon University, Tokyo, Japan

Abstract

The equations for obtaining the viscosities and melting points of ionic liquids were built. These equations could be applied imidazolium, pyridinium or ammonium cation with some kind of anions. Molecular descriptors for predicting viscosities and melting points of these ionic liquids were based on the size and electrostatic properties in the cations. To determine coefficients in none linear equation, genetic algorithm (GA) were adapted. Fourteen-parameter correlation was obtained for viscosity with $R^2 = 0.9464$. However, melting point correlation was hard to converge especially with BF_4 anion salts. In addition, we developed the prediction models of the viscosities, melting points, and electric conductivities by means of the group contribution method. Using this group contribution method, we developed reverse-design system which exhaustively generate ionic liquids structure corresponding to certain physical properties.

Introduction

Ionic liquids, which are salts that are liquids at ambient temperature, have been paid attention from many fields. Ionic liquids have the features of the salts, such as a high polarity, nonvolatile, flame resistance, heat hardiness, conductive property, etc. The melting point of ionic liquids is low, and they exist as a liquid even in the vicinity of the room temperature, while having the features as mentioned above. Using these features, ionic liquids are being applied to electrolysis solution for the battery, reactive solvent for green chemistry, lubricant agent, and catalyst, etc. Imidazolium, pyridinium, and tetra-alkyl ammonium derivative are used as a cation of ionic liquids. However, the synthesis of a variety of ionic liquids has been available easily, by using the neutralization with the triamine and the acid developed recently. When the molecular design of ionic liquids is performed, a lot of combinations, like the structure of the cation and anion, the length of the side chain, and the branch dividing structure, exist. In addition, the physical properties of ionic liquids changes according to the purity and water content. Therefore, serious differences of the properties are recognized among the literatures and catalogs of ionic liquids.

For the molecular design of these ionic liquids, the viscosity rises when the alkyl chain of the cation becomes long in the same compound group. Additionally, the value of melting point and viscosity decreases if the structure of the cation part becomes asymmetry. In previous studies concerning the correlation and prediction of melting points of ionic liquids, Katritzky et al. correlated the melting points of the bromoanion of imidazoles[1] and bromoanion of pyridiniums[2], respectively. We have reported the united analysis of the viscosities and melting points from the tetra-alkyl ammonium to the imidazorium with several anions[3].

In this study, the equations for obtaining the viscosity and melting points of ionic liquids were constructed using the technique of the computater chemistry and chemoinformatics. The surface area and volume of molecule, ovality, and the calculated results of molecular orbital were applied for the determination of these correlating equations (Figure 1). Estimation of properties for ionic liquids is very important, but in practical needs for industry, they eagerly want to know structures with certain properties. For example they want to know the structure which viscosity is lowest and electric conductance is highest. In such case, Molecular Orbital calculation based on QSPR is not appropriate. Therefore, we developed the prediction models of ionic liquid's properties by means of the group contribution method. We can easily build ionic liquid's structure on computer with using the group contribution. Then we can evaluate each structure. Such a reverse-design, that derives structure to take a value of a certain properties, was attempted, using this group contribution method developed in this study.

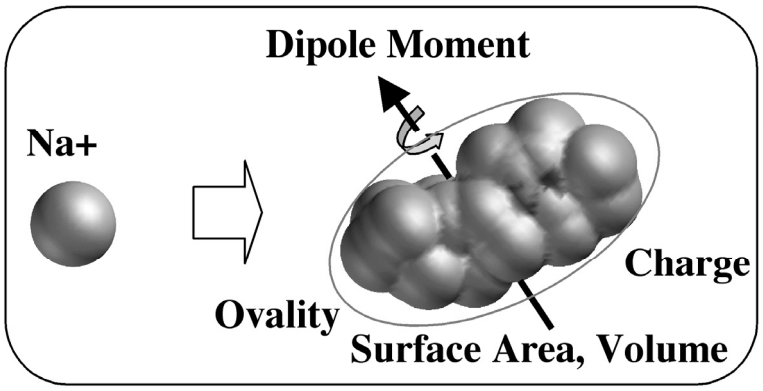

Figure 1. Molecular descriptors

Collection of Physical Properties of Ionic Liquids

The physical values of the ionic liquids were taken from the previous books[4, 5], and the catalogs of the ionic liquids[6 - 8]. Cation and anion of the ionic liquids considered in this study were as follows, cation: alkyl amine, pyrole, piperidine, pridine, imidazole, and pyrazole, anion: TFSI, Br, Cl, PF_6, BF_4, CF_3SO_3, CF_3BF_3, and $C_2F_5BF_3$. The side chain which attached to the cation was assumed to be $R_1 - R_4$. Table 1 is summarized the combinations of the cation and the anion, and the data points of the properties of ionic liquids, collected in this study.

Table 1. Combinations of Cation and Anion of Ionic Liquids Collected in this Study

	TFSI	Br	Cl	PF_6	BF_4	CF_3SO_3	CF_3BF_3	$C_2F_5BF_3$
alkylamine	36	0	0	0	5	0	6	6
Pyrole	11	0	2	1	1	1	0	0
piperidine	4	0	0	0	0	0	0	0
pyridine	3	4	3	3	4	1	0	0
Imidazole	10	12	15	14	16	10	6	6
Pyrazole	3	0	0	0	0	0	0	0

Calculation

Calculation of molecular descriptors

Calculation of the molecular descriptor for each cation was performed with the semiempirical molecular orbital method (MOPAC97) by means of Chem3D, Cambridge Soft Corporation. Dipole moment (DP), LUMO, charge on nitrogen atom (for the cation having two nitrogen, a larger charge is N_1), etc. was taken from the calculated results. As the value of LUMO was a minus with all compounds, the one that the sign of this value was reversed is written as LUMOM. After the structural optimization, the surface area, volume, and ovality of each cation were calculated by using Chem3D.

Construction of nonlinear prediction expression of viscosities and melting points

In this study, the following equation was applied for calculating the non linear property [P], assuming that P could be expressed as the multiplication of the exponential, that is, the most general, nonlinear fitting function.

$$\begin{aligned} \mathrm{P} = {} & \boldsymbol{C}_0 + \boldsymbol{C}_1 * (\boldsymbol{C}_{\boldsymbol{a}} * \mathrm{X_a} + \boldsymbol{C}_{\boldsymbol{b}} * \mathrm{X_b} + \cdots + \boldsymbol{C}_{\boldsymbol{i}} * \mathrm{X_i} + 1)^{\boldsymbol{\alpha}} \\ & \cdots \\ & * (\boldsymbol{C}_{\boldsymbol{m}} * \mathrm{X_m} + \cdots + \boldsymbol{C}_{\boldsymbol{q}} * \mathrm{X_q} + 1)^{\boldsymbol{\gamma}} \\ & \cdots \\ & * (\cdots + \boldsymbol{C}_{\boldsymbol{z}} * \mathrm{X_z} + 1)^{\boldsymbol{\omega}} \end{aligned} \tag{1}$$

C_0, C_z, and α to ω are the fitting parameters. In this study, the genetic algorithm (GA) were used to determine these parameters in none linear equation. Condition for GA is as follows: number of genes; 2000, generation number; 300000, mutation probability; 0.7, cross over probability; 0.2. Furthermore, the elite preserving was adopted.

Construction of Equations for Viscosities and Melting Points

Firstly, determined equation for expressing viscosities (Vis.) containing ionic liquids by the GA is as follows:

$$\begin{aligned} \log(\mathrm{Vis.}) = {} & 1.148 + 0.0830 * \\ & (-0.0122 * \mathrm{T_{ref}} + 1)^{0.397} * (-0.0069 * \mathrm{DP} + 1)^{0.664} * \\ & (0.1180 * \mathrm{LUMON} + 1)^{1.848} * \\ & (-0.1227 * \mathrm{Area} + 0.5272 * \mathrm{Vol.} - 28.6399 * \mathrm{Ova.} + 1)^{0.291} * \\ & (1.224 * \mathrm{N_1} + 0.0762 * \mathrm{N_2} + 1)^{1.213} * \\ & (-0.066 * \mathrm{TFSI} + \#\#\# * \mathrm{Br} + 1.354 * \mathrm{Cl} + 0.574 * \mathrm{PF_6} + 0.432 * \mathrm{BF_4} + \\ & 0.146 * \mathrm{CF_3SO_3} + 1)^{1.575} \end{aligned} \tag{2}$$

T_{ref} is the experimental temperature of ionic liquids. DP, LUMON, Area, Vol. and Ova. are the calculated molecular descriptor. N_1 and N_2 are the charge of nitrogen atom. The larger charge set to N_1 if cation has 2 nitrogen atom. If cation has only 1 nitrogen atom, N_2 set to 0. Set to 1 for corresponding anion, and the other anions are set to 0. In this study, the viscosity containing the Br anion was not

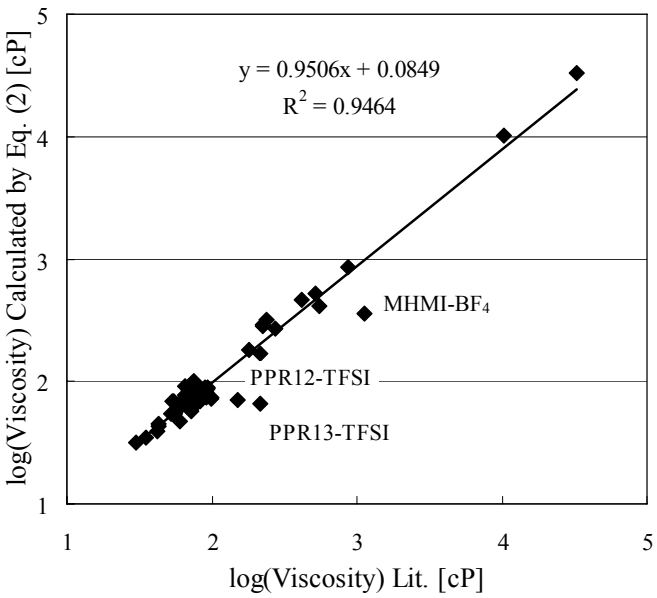

Figure 2. Calculated vs literature viscosities for the set of 62 ionic liquids.

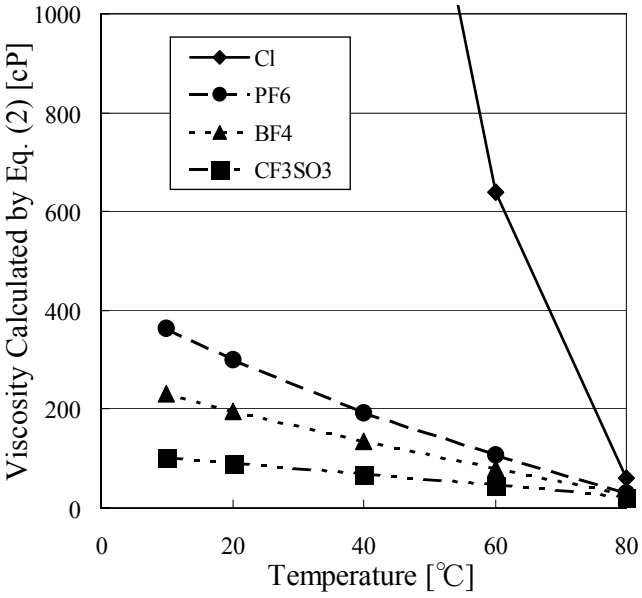

Figure 3. Temperature dependency of viscosities for BMI salts.

available. Therefore, the parameter concerning to the Br anion could not be determined. Correlated results by Eq. (2) are graphically shown in Figure 2. The value of the correlation coefficient R^2 was 0.9464. Therefore, Eq. (2) represents the experimental viscosities with good accuracy, while two piperidines (PPR) and MHMI-BF_4 deviate from the straight line.

By constructing this equation, it is possible to calculate the viscosities, freely changing the temperature (T_{ref}) and the anion. Figure 3 shows the calculated results when 1-butyl-3-methylimidazolium (BMI) was adopted as the cation. The experimental viscosities was cited from the book by Ono et al.[4] As can be seen in Figure 3, Eq. (2) gave the reasonable results at over 20 °C. Difference between the experimental and calculated viscosities at the low temperature is referred from no existence of the viscosities below 20 °C in the determination of the fitting parameters.

Secondly, determined equation for calculating melting points (T_m) is shown in Eq. (3):

$$
\begin{aligned}
T_m = {} & 4.967 + 119.985 * \\
& (0.00813 * \mathrm{DP} + 1)^{-3.2961} * (2.827 * \mathrm{LUMON} + 1)^{0.3262} * \\
& (-0.0441 * \mathrm{Area} + 0.0411 * \mathrm{Vol.} + 2.856 * \mathrm{Ova.} + 1)^{0.0497} * \\
& (0.406 * \mathrm{N_1} + 0.139 * \mathrm{N_2} - 1.056 * \mathrm{H_{max}} + 1)^{1.7334} * \\
& (-0.185 * \mathrm{dis.} + 1)^{-0.4598} * (0.555 * \mathrm{sym.} + 1)^{0.2209} * \\
& (-0.263 * \mathrm{TFSI} + 0.189 * \mathrm{Br} + 0.203 * \mathrm{Cl} - 0.00309 * \mathrm{PF_6} - 0.163 * \mathrm{BF_4} - \\
& 0.225 * \mathrm{CF_3SO_3} + 1)^{0.4923}
\end{aligned}
\tag{3}
$$

Figure 4 presents the correlated results by Eq. (3). In the prediction of melting points, there is no paragraph of T_{ref}. Instead, the charge of maximum charged proton (H_{max}), the distance from charged nitrogen atom to maximum charged proton (dis.), and the symmetry on charged nitrogen (sym.) are

needed, as well as the molecular descriptors. Requirement of these information shows that the hydrogen bond between anion and hydrogen changes the melting points. Therefore, hydrogen bond evaluation became important for melting points. Calculation accuracy for Cl and Br, that is, anion is small, is high. From Eqs.(2) and (3), we can easily find out how the dipole moment works to viscosity or melting point. If dipole moment of cation increase, then viscosity and melting point decrease. To increase dipole moment, the charge plus center should shift from molecular center. The more get away, the more dipole moment increase, and the size of cation also increase. The size effects contribute to increase viscosity and melting point calculated by the term of Area,Volume and Ovality. So, the balance of dipole moment effect and molecular size effects determine ionic liquid properties. We can evaluate these effects quantitatively with Eqs.(2) and (3).

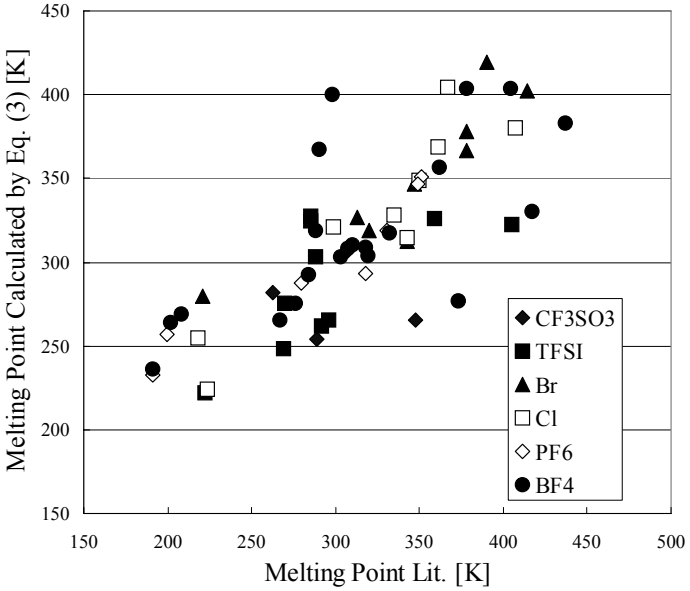

Figure 4. Calculated vs literature melting point for the set of 60 ionic liquids.

Group Contribution Method and Reverse-Design of Ionic Liquids

In this study, the prediction model for the properties of ionic liquids (viscosity, melting point, and electric conductivity) was developed by means of the group contribution method. As an example of

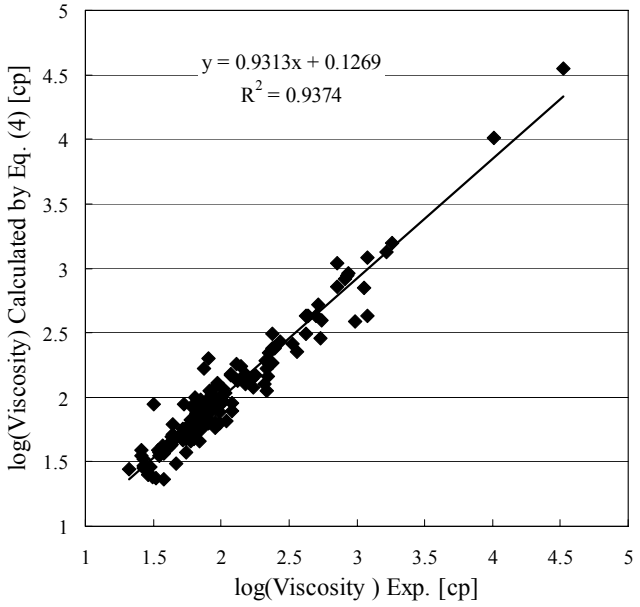

Figure 5. Correlation between experimental viscosity and calculated by Eq. (4).

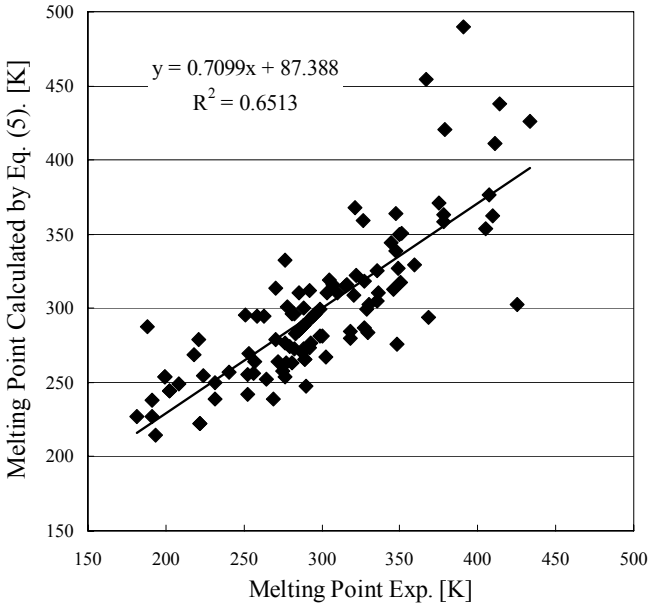

Figure 6. Correlation between experimental melting point and calculated by Eq. (5).

the prediction models constructed in this study, the equation for expressing viscosities is given in the following Eq. (4).

$$\begin{aligned}\log(\mathrm{Vis.}) = {} & 0.562 + 1.368 * \\ & (0.036 * \mathrm{T_{ref}} + 1)^{-4.040} * \\ & (0.729 * \mathrm{alkylamine} + 1.131 * \mathrm{pyrole} + 2.048 * \mathrm{piperidine} + \\ & 1.040 * \mathrm{pridine} + 0.899 * \mathrm{imidazole} + 0.619 * \mathrm{pyrazole})^{0.617} * \\ & (0.848 * \mathrm{R_1} + 0.465 * \mathrm{R_2} + 4.559 * \mathrm{R_3} + 2.442 * \mathrm{R_4} + 1)^{0.343} * \\ & (0.572 * \mathrm{TFSI} + 2.464 * \mathrm{Br} + 2.602 * \mathrm{Cl} + 1.289 * \mathrm{PF_6} + \\ & 1.046 * \mathrm{BF_4} + 0.791 * \mathrm{CF_3SO_3} + 0.500 * \mathrm{CF_3BF_3} + 0.580 * \mathrm{C_2F_5BF_3})^{0.725}\end{aligned} \tag{4}$$

Eq. (4) calculates the viscosity on the basis of the T_{ref} and the number of cation (alkylamine, pyrole, … , pyrazole), side chain (R_1, R_2, … , R_4), and anion (TFSI, Br, Cl, … , $C_2F_5BF_3$). Figure 5 illustrates the deviation of the calculated results and the experimental values. As can be seen from Figure 5, the value of the correlation coefficient R^2 was 0.973, and this prediction model of viscosity gave excellent results.

Similarly, the prediction model of melting points is also presented in Eq. (5).

$$\begin{aligned}\mathrm{T_m} = {} & 95.388 + 6.451 * \\ & (0.102 * \mathrm{alkylamine} + 0.086 * \mathrm{pyrole} + 0.098 * \mathrm{piperidine} + \\ & 0.139 * \mathrm{pridine} + 0.120 * \mathrm{imidazole} + 0.125 * \mathrm{pyrazole})^{-0.966} * \\ & (0.021 * \mathrm{R_1} + 0.086 * \mathrm{R_2} - 0.059 * \mathrm{R_3} + 0.019 * \mathrm{R_4})^{-0.558} * \\ & (0.677 * \mathrm{TFSI} + 0.092 * \mathrm{Br} + 0.071 * \mathrm{Cl} + 0.204 * \mathrm{PF_6} + \\ & 0.549 * \mathrm{BF_4} + 0.268 * \mathrm{CF_3SO_3} + 0.560 * \mathrm{CF_3BF_3} + 0.676 * \mathrm{C_2F_5BF_3})^{-0.183}\end{aligned} \tag{5}$$

Correlated results are given in Figure 6. This correlation was obtained with $R^2 = 0.6513$, and the correlation accuracy is inferior to the results of the viscosities. However, qualitative representation of melting points was possible.

In this study, the reverse-design of ionic liquids was tested using these equations by using the constructed prediction models. As an example, the structure of cation and the combination of anion, which, at 25 °C, the value of the viscosity and electric conductivity enter 30 cp and 10 mS/cm, respectively, were designed. Figure 7 shows the screen shot of our ionic liquids design system. This reverse-design first selects a basic frame of the cation, and selects the anion. Then, the viscosity and electric conductivity are calculated by each prediction model changing the number of side chains. Finally, the combinations that enter the target value are listed. As a result, 10 kinds of combination were found. These

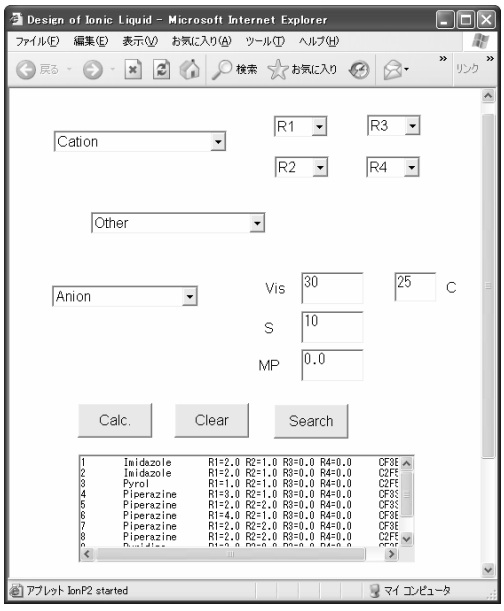

Figure 7. Screen shot of our ionic liquids design system.

combinations are listed in Table 2. By using this technique, it is possible to search the candidates when the temperature is changed. In this study, collected data of electric conductivities for the determination of fitting parameters are only in 25 °C, and the temperature dependency is not considered in the prediction model for the electric conductivities. However, this method can be said to give a very useful solution for covering with a computer, while it is powerless to a completely new structure.

Table 2. Results of Reverse-Design of Ionic Liquids

No.	Cation	Side chain	Anion
1	Imidazole	$R_1 = 2.0\ R_2 = 1.0\ R_3 = 0.0\ R_4 = 0.0$	CF_3BF_3
2	Imidazole	$R_1 = 2.0\ R_2 = 1.0\ R_3 = 0.0\ R_4 = 0.0$	$C_2F_5BF_3$
3	Pyrol	$R_1 = 1.0\ R_2 = 1.0\ R_3 = 0.0\ R_4 = 0.0$	$C_2F_5BF_3$
4	Piperazine	$R_1 = 3.0\ R_2 = 1.0\ R_3 = 0.0\ R_4 = 0.0$	CF_3SO_2
5	Piperazine	$R_1 = 2.0\ R_2 = 2.0\ R_3 = 0.0\ R_4 = 0.0$	CF_3SO_2
6	Piperazine	$R_1 = 4.0\ R_2 = 1.0\ R_3 = 0.0\ R_4 = 0.0$	CF_3BF_3
7	Piperazine	$R_1 = 2.0\ R_2 = 2.0\ R_3 = 0.0\ R_4 = 0.0$	CF_3BF_3
8	Piperazine	$R_1 = 2.0\ R_2 = 2.0\ R_3 = 0.0\ R_4 = 0.0$	$C_2F_5BF_3$
9	Pyridine	$R_1 = 2.0\ R_2 = 0.0\ R_3 = 0.0\ R_4 = 0.0$	CF_3BF_3
10	Pyridine	$R_1 = 2.0\ R_2 = 0.0\ R_3 = 0.0\ R_4 = 0.0$	$C_2F_5BF_3$

Conclusion

The correlation models for the properties of ionic liquids were developed. Firstly, the correlation models for viscosities and melting points were determined on the basis of the surface area and volume of molecule, ovality, and the dipolemoment so on. The correlated results showed the molecular size effects and dipolemoment effect quantitatively. These results help us understand fundamental properties of ionic liquid. Secondly, we constructed the prediction models by using the group contribution method. The prediction accuracy using these models was slightly inferior to the ones using the structure properties mentioned above. However, these models based on group contribution were useful for the reverse-design of ionic liquids. The proposal of exhaustively covering candidate structure became possible by using these prediction models.

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