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Predicting the Decomposition Temperature of Ionic Liquids by the Quantitative Structure–Property Relationship Method Using a New Topological Index

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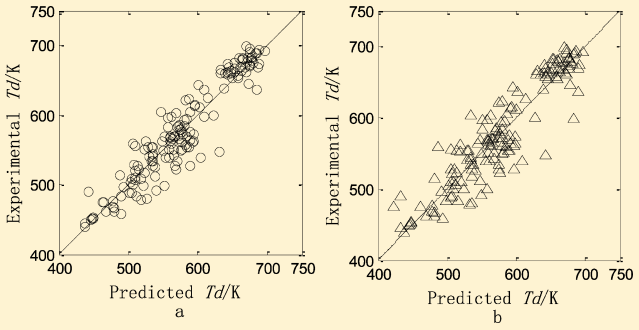
Supporting Information

ABSTRACT: In this work a new topological index (TI) was proposed based on atom characteristics (e.g., atom radius, atom electronegativity, etc.) and atom positions in the hydrogen-suppressed molecule structure. Using the TIs, a multiple linear regression (MLR) model was developed for predicting the decomposition temperature (T_d) of 158 ionic liquids (ILs), which are based on imidazolium, pyridinium, pyrrolidinium, ammonium, phosphonium, sulfonium, and guanidinium. Because ILs are a class of molten salts which are composed entirely of cations and anions, in general, the descriptors for ILs are calculated from cations and anions separately, and the interaction between them is neglected. In this study, except for the two sets of TIs generated from cations and anions, a third TI was proposed to depict the interaction of anions and cations. The regression coefficient (R^2) and the overall average absolute deviation (AAD) are 0.893 and 3.07 %, respectively.



INTRODUCTION

Ionic liquids (ILs) have attracted much attention in recent years, for their beneficial properties such as negligible vapor pressure, high heat capacity, high density, high thermal conductivity, high thermal stability, a wide temperature range for liquids, and so on. The most interesting character is that the properties of ILs could be altered by modifying the structures of their cations or anions, which increases the unique features and applicability of ILs further. Due to the advantages mentioned above, ILs have a diversity of applications: electrolytic media,[1−3] catalysis,[4−6] solvents,[7−10] and telescope construction.[11]

To extend the applications of ILs and design new potential ILs, the fundamental understanding of the physical and chemical properties of ILs is essentially important. Some basic property data are available from some databases and literature. The International Union of Pure and Applied Chemistry (IUPAC) ILs Database[12] is a free database that allows users to access an up-to-date data collection from publications on experimental investigations of thermodynamics and transport properties of ILs. The Beilstein database is one of the largest databases in the field of organic chemistry including ILs.[13] The Dortmund Data Bank is also a useful database for ILs.[14] Although these databases and literature are available, there is not a comprehensive database publicly available for researchers to consult[15] due to the lack of experiments for the large number of kinds of ILs. Therefore, it is necessary to develop available mathematical models to predict the properties of ILs.

ILs have large liquid ranges determined by their low melting points as well as a high decomposition temperature (or boiling point). ILs either undergo a boiling point or decomposition point upon heating.[16] As an idea of the upper operating range of the fluids, decomposition temperature is an essential physical property for ILs. The decomposition point is necessary to value the thermal stability which could expand the application of ILs. No model has been reported on predicting the decomposition temperature of ILs.

The quantitative structure–property relationship (QSPR) method provides a sophisticated approach to the study of physical properties. Some QSPR models have been developed for predicting the properties of ILs. Most work has been focused on predicting the melting points of ILs.[17−29] There are also QSPR models estimating other properties of ILs: viscosity,[30,31] surface tension,[32] and ionic conductivity.[33] The QSPR method can predict the physical properties of compounds with similar structural features accurately. In this work, a new topological index (TI) was proposed only using the atom characters and atom positions in the hydrogen-suppressed structure of molecule.

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The TIs are not only generated from cations and anions but also from their interaction. Then a QSPR model was derived for predicting the decomposition temperature of ILs with the TIs.

METHODS

Data Set. A total of 158 ILs were used for developing the QSPR model, which includes 43 imidazolium (Im), 18 pyridinium (Pyi), 14 pyrrolidinium (Pyo), 45 ammonium(Am), 4 phosphonium (Ph), 18 sulfonium (Su), and 16 guanidinium (Gu). All of the data are obtained from 14 references.[34−47]

Topological Index. Topological indexes (TIs) are numerical quantities derived from a graphical theoretical representation of the molecular structure through mathematical invariants.[48] There are two main sources of TIs—the distance (D) and adjacency (A) matrixes, which are defined as:

$$D = (d_{ij})$$

$$d_{ij} = \begin{cases} n & \text{if the path length between atoms i and j is } n \\ 0 & \text{otherwise} \end{cases} \quad (1)$$

$$A = (a_{ij})$$

$$a_{ij} = \begin{cases} 1 & \text{if the path length between atoms i and j is 1} \\ 0 & \text{otherwise} \end{cases} \quad (2)$$

Wiener[49] proposed the first TI/Wiener index W, from distance matrix D. The Wiener index W is one of the most widely used TI. It is defined as the sum of the elements in a distance matrix. More and more TIs have been developed from then on: Schultz's molecular topological index MTI,[50] Randic's molecular connectivity index χ,[51] Pakmakar's PI index,[52] Balaban's J index,[53] and Hosoya's Z topological index.[54] The above processes only take into account the route between apexes and the adjacency relationship of the apexes. The type of atom and bond is neglected; therefore it will be difficult to show the adjacency of the C atom with other heteroatoms, which do limit its field of applications.

Some TIs have been proposed for resolving the heteroatom differentiation. Ren[55] derived atom-type AI TIs from the topological distance sums and vertex degree which are further used to describe different structural environments of each atom type in a molecule. Kier and Hall[56] developed the ${}^{m}\chi$ index, which introduced the concept of valence connectivities to differentiate heteroatoms using the valence electrons of each atom in the molecule. Estrada[57] proposed a possible solution to the problem of differentiation of heteroatoms in molecular graphs by using weights in the nondiagonal entries of the edge adjacency matrix.

Yao et al.[58] generated three TIs from path matrixes A, B, and C and two vectors (V), V_1 and V_2. The three TIs provided a sophisticated way to distinguish heteroatoms. They are defined as:

$$B = (a_{ij})$$

$$a_{ij} = \begin{cases} 2 & \text{if the path length between atoms i and j is 2} \\ 0 & \text{otherwise} \end{cases} \quad (3)$$

$$C = (a_{ij})$$

$$a_{ij} = \begin{cases} 3 & \text{if the path length between atoms i and j is 3} \\ 0 & \text{otherwise} \end{cases} \quad (4)$$

$$V_1 = (a_i) \quad (5)$$

a_i is the square root of vertex degree of atom i.

$$V_2 = (a_i) \quad (6)$$

a_i is the square root of the van der Waals radii of atom i.

Then three TIs are defined as

$$A_1 = \lambda_{max_1}/2 \qquad A_2 = \lambda_{max_2}/2 \qquad A_3 = \lambda_{max_3}/2 \quad (7)$$

where λ_{max1} to λ_{max3} are the largest eigenvalues of matrixes Z_1 to Z_3, which are defined as

$$Z_1 = [A\ V_1\ V_2] \times [A\ V_1\ V_2]^T \quad (8)$$

$$Z_2 = [B\ V_1\ V_2] \times [B\ V_1\ V_2]^T \quad (9)$$

$$Z_3 = [C\ V_1\ V_2] \times [C\ V_1\ V_2]^T \quad (10)$$

Although so many TIs have been proposed, there is no general TI that can be used for ILs separately. In this work a new TI is proposed based on Yao's method[58] mentioned above to solve this problem.

New TI. There are two steps to generate the TI. First, obtain the information of molecule and set it in a total matrix (TM), which is generated from the distance matrix D and character vector (CV). Instead of matrixes A, B, and C, D is used for determining the positions of atoms in a molecule, because D contains much more position information than A, B, and C matrixes. The CV is used for determining the characters of atoms in the hydrogen-suppressed molecule. For each TM only one CV is used, and nine CVs are defined.

TM is defined as

$$TM = [D\ CV] \times [D\ CV]^T \quad (11)$$

Every atom in the hydrogen-suppressed graph is first numbered randomly with different numbers from 1 to N, which is the total number of non-hydrogen atom in the molecule. CV is defined as:

$$CV = (a_i) \quad (12)$$

a_i is the element that characterize the atom i.

To depict the molecule all eight-sided CVs are defined using eight elements. They are defined as follows:

CV_1, a_i: $\pi \times$ van der Waals radii;

CV_2, a_i: atom weight;

CV_3, a_i: atom electronegativity;

CV_4, a_i: $\pi \times$ atom radius;

CV_5, a_i: exp(vertex degree, defined as the number of adjacent atoms);

CV_6, a_i: exp(fraction of hydrogen to atom i and hydrogens adjacent to it);

CV_7, a_i: exp(1/atom electronic shell number);

CV_8, a_i: exp(1/atom outermost electron number).

Another CV is defined as:

CV_9, a_i: 0, which means no element.

The values of van der Waal radii, atom radius, and electronegativity for all atoms are listed in Table 1.

Second, calculate TI from TM. The eigenvalues of TM are calculated first. Then four TIs are obtained from the eigenvalues.

Four TIs are defined as:

$$TI_1 = \sum \tanh(\lambda_i) \quad (13)$$

$$TI_2 = \sum \lambda_i \quad (14)$$

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Table 1. Van der Waals Radii, Atom Radius, and Electronegativity for All Atoms Used in This Work

atom	B	C	N	O	F	S	P	Cl	Br	I
van der Waals radii (Å)	0.98	1.8	1.5	1.4	1.35	1.85	1.9	1.85	1.95	2.15
atom radius (Å)	1.17	0.91	0.75	0.65	0.57	1.09	1.23	0.97	1.12	1.32
electronegativity	2.04	2.55	3.04	3.44	3.98	2.58	2.19	3.16	2.96	2.66

Table 2. Parameters and Types of TIs for Equation 18[a]

TI type			$TI_{Ca,i}$		$TI_{An,j}$		$TI_{To,h}$	
m	*k*	*n*	i	$\alpha_{Ca,i}$	j	$\alpha_{An,j}$	h	$\alpha_{To,h}$
1	1	5					1	51.15234
2	1	5	1	119.1479				
	4				1	42.27335		
3	2	5	2	0.198191				
	3		3	−0.19077				
4	2	5	4	−9.71729				
	4		5	865.373				
5	2	5	6	0.032891			2	−4.63978
	3		7	0.069241	2	0.008505		
	4		8	−0.96874				
6	2	5			3	−75.3089	3	−792.579
	3				4	67.35157		
	4				5	270.8507		
7	1	5			6	−224.412		
	4		9	9325.557	7	−313.48		
8	2	5	10	9.62628			4	747.9859
	4		11	−10191.3				
9	1	5			8	248.7957		
	2				9	75.68239		
	3				10	−67.8251		

[a] *m*: TI is obtained from TM generated from CV_m and *D*; *k*(1−4): $TI_{Ca,i}$ or $TI_{An,i}$ is defined as eqs 13 to 16. *n*(5): $TI_{To,h}$ is defined as eq 17.

$$TI_3 = \max(\lambda_i) \tag{15}$$

$$TI_4 = \text{mean}(\lambda_i) \tag{16}$$

where λ_i are the eigenvalues of TM.

According to eqs 13 to 16, one TM will generate four TIs. For one set, there are 36 TIs obtained from 9 TMs generated from 1 *D* and 9 CVs. Because ILs are composed entirely of cations and anions, two sets of TIs are generated from cations and anions by the method mentioned above, respectively.

The decomposition temperature of IL is not the simple sum of anion and cation contributions; therefore another set of TI is proposed for depicting the interaction of cations and anions.

TI is defined as:

$$TI_5 = \sqrt{\sum \lambda_{Ca,i} + \sum \lambda_{An,i}} \tag{17}$$

where $\lambda_{Ca,i}$ and $\lambda_{An,i}$ are the eigenvalues of TMs from cations and anions, respectively.

According to eq 17 another set of 9 TIs are obtained from 9 TMs generated from cations and 9 TMs generated from anions. The detailed procedure for calculating the three sets of TIs is shown in the Supporting Information by the example of 1-ethyl-3-methylimidazolium methylsulfate.

RESULTS AND DISCUSSION

For each ILs, three sets of TIs containing 36, 36, and 9 TIs are generated from cations, anions, and their interaction, respectively. After many calculations, it was found that, for the 81 TIs, some of them contain little valid information and they cannot improve the prediction precisely. To simplify the model, some of these TIs containing little valid information can be omitted, and only the more valid TIs are selected to develop the QSPR model. After attempting many calculations, 11, 10, and 4 TIs selected from the cation set, anion set, and their interaction set were used to develop the QSPR model. A MLR model was developed as:

$$P = P_0 + a\sqrt{NN_{cat}} + \sum_{11}^{i=1} \alpha_{Ca,i} \cdot TI_{Ca,i} + \sum_{10}^{j=1} \alpha_{An,j} \cdot TI_{An,j} + \sum_{4}^{h=1} \alpha_{To,h} \cdot TI_{To,h} \tag{18}$$

$$N = 158 \qquad R^2 = 0.893 \qquad F = 41.47$$

$$\text{AAD} = 3.07\ \% \qquad \text{AAE} = 17.38\ \text{K}$$

where *P* is the predicted decomposition temperature; $TI_{Ca,i}$, $TI_{An,j}$, and $TI_{To,h}$ are TIs generated from cations, anions, and their interaction, respectively; NN_{cat} is non-hydrogen atom number of cations. P_0, *a*, $\alpha_{Ca,i}$, $\alpha_{An,j}$, and $\alpha_{To,h}$ are parameters. P_0 and *a* are −14421.8 and −218.9287, respectively. Other parameters and the type of TIs are shown in Table 2.

$$\text{AAE} = \frac{\sum |T_{d,Exp} - T_{d,Cal}|}{n} \tag{19}$$

$$\text{AAD} = \frac{1}{n} \cdot \sum \frac{|T_{d,Exp} - T_{d,Cal}|}{T_{d,Exp}} \cdot 100\ \% \tag{20}$$

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Table 3. Overall Results of the MLR Model

chemical family	Im	Pyi	Pyo	Am	Ph	Su	Gu	overall
no. of samples	43	19	14	45	4	18	16	158
AAD·100	4.14	3.77	3.54	2.60	1.13	2.16	1.87	3.07

where n is number of samples; $T_{d,Exp}$ and $T_{d,Cal}$ are the experimental and calculated decomposition temperature values, respectively.

The overall calculation results of the model for each chemical family are shown in Table 3. The overall AAD is 3.07 %, among which the AAD of ammonium-, phosphonium-, sulfonium-, and guanidinium-based ILs is small and the AAD of other three kinds of chemicals is relatively bigger than the overall AAD, which is because imidazolium-, pyridinium-, and pyrrolidinium-based ILs contain more anion types. The calculated values by eq 18 and the experimental data of decomposition temperature are compared in Figure 1. Also, the AAD distribution is schematically shown in Figure 2. The AAD for most of the samples is smaller than 5 %.

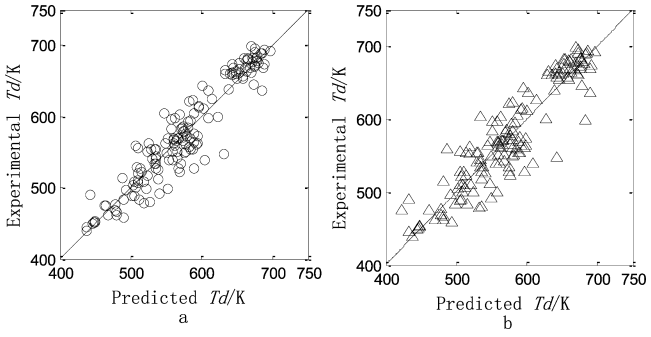

Figure 1. Comparation of the predicted decomposition temperature (T_d/K) by the model (a) and leave-one-out cross-validation (b) with the experimental T_d/K.

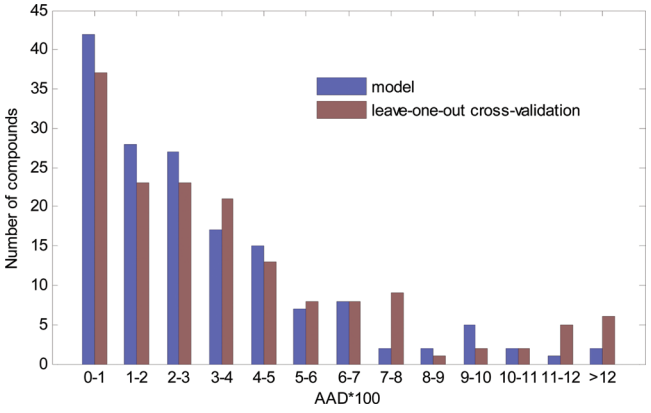

Figure 2. Distribution of the AAD by the model and leave-one-out cross-validation.

In all, it can be found that it is reliable for calculating the decomposition temperature by eq 18. The experimental data and the calculated values by eq 18 for decomposition temperature are shown in the Supporting Information. Also the $TI_{Ca,i}$, $TI_{An,j}$, and $TI_{To,h}$ are presented as the Supporting Information.

The predicting ability of the model is checked by leave-one-out cross-validation and external validation.

Leave-One-Out Cross-Validation. The results of leave-one-out cross-validation are shown in Table 4. The results show that the R^2, AAD, and AAE are accepted although are not as good as eq 18. The calculated values by leave-one-out cross-validation and the experimental data of decomposition temperature are compared in Figure 1. Also, the AAD distribution of leave-one-out cross-validation is compared with AAD distribution of eq 18, which is shown in Figure 2. From Figure 2, it can be found that the AAD distribution of leave-one-out cross-validation is almost the same with that of eq 18, which means a good predicting ability of eq 18.

Table 4. Result of Predicting Ability Test by Leave-One-Out Cross-Validation

status	no. samples	R^2	AAE	AAD·100
model	158	0.893	17.38	3.07
leave-one-out cross-validation	158	0.842	21.29	3.78

External Validation. The data set is randomly divided into the training set (126) and testing set (32): then the QSPR model is developed using the samples in the training set by the same TI with eq 18 and the samples predicted in the testing set by this model. R^2, AAD, and AAE for the training set and testing set are calculated, and they are listed in Table 5. From Table 5, it can be found that the R^2 in the training set and in the testing set is approximate to the overall R^2. The AAE and AAD in the training set are also approximate to the overall AAE and AAD; AAE and AAD in the testing set are a little bigger than the overall AAE and AAD. The calculated values in traning set and the experimental data of decomposition temperature are compared in Figure 3. The calculated values in testing set and the experimental data of decomposition temperature are also compared in Figure 3. The overall results show that this method has a good predictive ability.

Table 5. Result of the Predicting Ability Test by External Validation

status	no. samples	R^2	AAE	AAD·100
training set	126	0.888	17.68	3.11
testing set	32	0.888	19.46	3.53

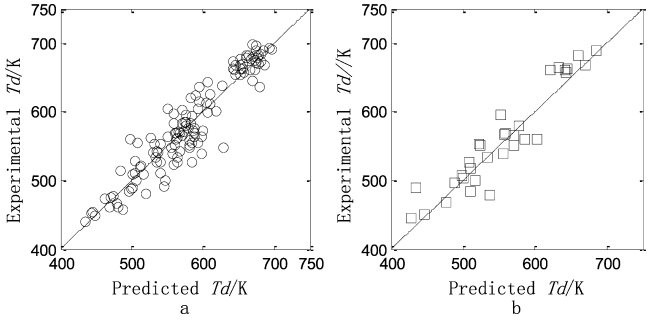

Figure 3. Comparation of the predicted decomposition temperature (T_d/K) by the training set (a) and testing set (b) in external validation with the experimental T_d/K.

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CONCLUSIONS

In this work, a TI was proposed from the atom characters (e.g., atom radius, atom electronegativity, etc.) and atom positions in the hydrogen-suppressed molecule structure. A MLR model for predicting the decomposition temperature of ILs was developed by three sets of TIs generated from cations, anions, and their interaction. In the model, not only the contributions of cations and anions but also the interactions of cations and anions were considered, which is distinguished from the ordinary QSPR models. Using this model, the decomposition temperature of 158 ILs was calculated, and the overall values of R^2 and AAD for the model are 0.893 and 3.07 %, respectively. At the same time, the results of the predictive calculations show that the model has a good predictive ability. All of the results show that the TI proposed in this work is not only simple but also efficient for predicting the decomposition temperature of ILs.

ASSOCIATED CONTENT

Supporting Information

The detailed procedure for calculating the three sets of TIs by the example of 1-ethyl-3-methylimidazolium methylsulfate (pdf); the experimental and predicted decomposition temperature data and the TIs used in eq 18 (xls). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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