Development of Generalized Correlation for Electrical Conductivity Prediction of Pure Ionic Liquid

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Abstract: Ionic liquids are salts in liquid form that are composed of short-lived ion pairs. They are the new trend of solvent because of their very low vapor pressure, good chemical and thermal stability, and melting temperatures lower than 100°C. Pure ionic liquids contain ions that can conduct electricity or serve as electrolytes. But experimentation using ionic liquids would be expensive. This study aims to develop a generalized correlation for the electrical conductivity prediction of pure ionic liquids. The researchers gathered data of pure ionic liquids that involved the electrical conductivity property from the ThermoIL Database. The collected data were then trimmed based on a developed scheme and classifications. After trimming the data, the researchers evaluated the data using MATLAB software. The residual value was calculated, and a parity plot was constructed to test the models' accuracy. The researchers gathered 2,425 data points from 310 references and were trimmed to 220 data points from 21 references. The parity plot and graph of the residuals plotted against pressure showed that the experimental and calculated values were close. Results showed that the electrical conductivity of pure ionic liquids could be predicted using a model patterned to Pitzer correlation with reduced temperature and reduced pressure as variables. Data with two or more references and low uncertainty made a good result on the models to create a generalized correlation via curve fitting.

Key Words: pure ionic liquids; electrical conductivity; generalized correlation; data trimming; data mining

1. INTRODUCTION

Ionic liquids (ILs) are liquid salts that are composed of ions and short-lived ion pairs. ILs are potential substitutes for dangerous solvents for preparing solutions such as gels, composites, and polymeric belts (Shakeel et al., 2019). Some of the interesting properties of ILs include Chemical and thermal stability, very low vapor pressures, and melting temperatures below 100°C. In 1914, Paul Walden was the first to find ILs. Walden was looking for liquid molten salts at a specific temperature to use in his equipment without fulfilling any specifications. The melting point of ethylammonium nitrate (EtNH3NO3), the first IL found, is 12°C, according to Walden (Welton, 2018). ILs are also environmentally friendly, easily recyclable, highly efficient, and similarly structured to conventional solvents. As a result, these liquids have become the latest solvent standard.

The electrical conductivity of ILs is also an intriguing property. Electrical conductivity (σ), also known as conductance, is the potential of a material to bear an electric current (Helmenstine, 2020). Based on the temperature, each liquid material has a different conductance. Electrical conductivity increases by two to three percent with every one-degree Celsius increase in temperature. Between liquid substances, pure water has the lowest conductivity. That is primarily due to the low number of ions present in pure water. ILs, in contrast, have many ions that are essential in conductance. An aqueous substance's conductivity increases as the number of ions present increases, indicating a solid electrolyte. Thus, ILs are used in commercial devices as an electrolyte with longer battery life because of their low vapor pressure.

Conducting experiments or research utilizing ionic liquids would be expensive. One of the cheapest IL in the market is the Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate, which costs $21 (approximately Php 1066.50) for five grams. This is the main reason why most researchers do data mining rather than doing experiments. Data collected by experimental procedures of previous researchers are collected and compiled on a database accessed on the internet. These data, however, are not being utilized well. Data mining is the process of discovering correlations, patterns, and trends using pattern recognition technologies and statistical and mathematical techniques (Gartner Group, 2014). This process is an efficient way to utilize available data on the internet. There are different data mining methods, and each has different uses depending on the situation, which can help businesses and researchers (Loginworks Software, 2014).

This research aims to develop a generalized correlation for the prediction of the electrical conductivity of pure ionic liquids. It also seeks to determine the most suitable data available from literature (ThermoIL Database) using the data trimming process and create the generalized correlation via-curve fitting the data using the MATLAB Software. This study, on the other hand, will help other researchers develop their research, especially those who have similar topics to this study. Furthermore, manufacturers can also innovate new products and find an ionic liquid that can serve as an electrolyte and improve its quality using this mathematical model.

This study solely aims to create a correlational model that can help predict the electrical conductivity of pure ILs. It does not cover the uses of knowing the electrical conductivity of ILs; it will only serve as a stepping stone to other researchers that plan to create commercial applications from pure ILs. This study will also gather data from the ThermoIL database only. The researchers will be cross-referencing, and they will use the data to create a correlational model for predicting pure IL's electrical conductivity. The study will not perform any laboratory experiments to justify the claims. The study will not include binary mixtures and tertiary mixtures, and ILs that do not have standard pressure.

2. METHODOLOGY

2.1 Collection of Data from ThermoIL database

The researchers first collected data. These data were collected from the ThermoIL database, covered pure ionic liquids, and focused on an ionic liquid's electrical conductivity property. The researchers also gathered the chemical structures for each of the chemical formulas for its visual representation. Each IL was given codes according to their cation and anion. The researchers obtained the International Union of Pure and Applied Chemistry (IUPAC) name of the pure IL, molar weight in terms of grams per mole (g/mol), pressure in terms of kilopascal (kPa), the temperature range in terms of Kelvin (K), electrical conductivity range in terms of siemens per meter (S/m), and its reference.

2.2 Data Trimming

The researchers gathered data of pure ILs reporting electrical conductivity from all available literature in the ThermoIL database. All of the data gathered from experimental procedures have been assessed carefully to ensure only accurate and reliable data will be collected and used since this research will only conduct computational methods. Figure 1 shows a developed scheme for the data trimming process and was classified into three categories as follows; (i) systems with more than two available references, (ii) systems with two available references, and (iii) systems with only one reference. Different data trimming procedures were done in each category. The data from the systems with more than two references had been trimmed by only using the most consistent data with the other references. For systems with two references, the most accurate between them was chosen based on the uncertainty reported. Systems with only one reference had been considered automatically; however, systems that only have two or fewer data points were removed and were not considered. Trimmed data were then investigated to gather the cations and anions (Soriano, Agapito, Lagumbay, Caparanga & Li, 2010).

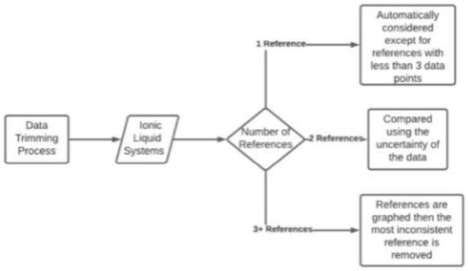


Figure 1. *Data trimming flowchart*

2.3 Development of Generalized Correlation for Electrical Conductivity

The researchers created a mathematical model. It was used to predict the electrical conductivity of a pure ionic liquid. The model used is patterned to the general Pitzer correlation to fit electrical conductivity, σ, as a function of temperature, T. It is represented as:
= T0+ T1 (Eq. 1) where ω is the acentric factor for the ionic liquid. For this study, the parameters T0 and T1

were defined as quadratic functions of the temperature:
To=A1+ A2TTc+ A3TTc2
(Eq. 2)
T1=A4+ A5TTc+ A6TTc2
(Eq. 3)

The ratio of T and Tc is the reduced temperature, where Tc is the critical temperature of the ionic liquid. Empirical constants were represented as An (n = 1 to 6), and acentric factors and critical data were obtained from the paper of Valderrama, Forero, and Rojas (2012). Pitzer's equations are used to describe the activity coefficients of aqueous electrolytes.

2.4 Testing of Model

The researchers tested the model's accuracy by finding the distance between the experimental (literature) data and calculated (predicted) data. It was determined using the Residual as follows:

Residual = y - y

(Eq. 4) where y is the experimental electrical conductivity and y is the calculated electrical conductivity.

The researchers also created a parity plot, a plot used to compare experimental or literature values to the calculated or tabulated values. Its purpose is to determine whether the obtained values are acceptable or not.

3. RESULTS AND DISCUSSION

The researchers were able to collect the data needed in this research from the ThermoIL database. They have collected 2,425 data points from 310 reference studies, which observed the criteria required. The gathered electrical conductivity of pure ILs from the database were all under standard pressure and are in the liquid phase.

The data collected underwent a data trimming process to remove unnecessary and insignificant data. ILs were grouped for data trimming according to the number of references available. References with less than three data points were first removed from all the groups of ILs. The data with only one reference was retained, while for those with two references, the data with high uncertainty were removed. The data with more than two references were plotted in a graph. The data that do not fit the dataset was then removed. Figure 2 shows an example of a graph used in the data trimming process for ILs with more than two references. The reference that contains the yellow points was removed from the dataset.

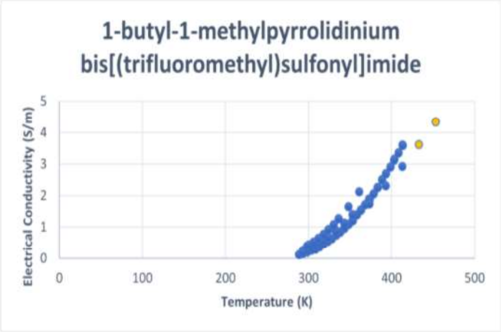


Figure 2. *Example of data trimming for ILs with more than two references*

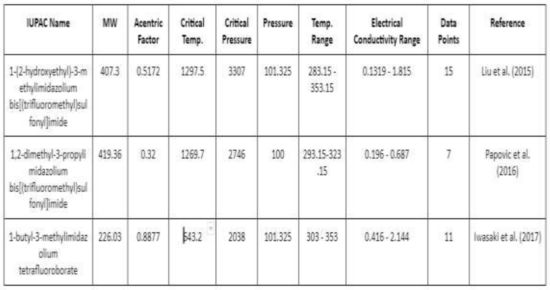
The data trimming process reduced the number of data points and references to 2,231 and 203, respectively. Due to data unavailability, the numbers were cut off again after the researchers gathered the acentric factors and critical constants needed for the process. ILs with incomplete factors and constants were removed, decreasing the number of data points and references to 220 and 21, respectively. Table 1 shows the summary of the trimmed data used to develop the generalized correlation.

In using MATLAB software, equations 2 and 3 were manipulated to reduce the deviation of the experimental data and calculated data. Equations 5 and 6 show the new equations used in the process with the addition of pressure and critical pressure values. Figure 3 shows the parity plot that displays the relationship between the experimental and calculated data. It shows that most of the data points are near the line of equality, indicating that most of the calculations are close to experimental values.

$$T^{o} = A_1 + A_2\left(\frac{T}{T_c}\right) + A_3\left(\frac{T}{T_c}\right)^2 + A_4\left(\frac{P}{P_c}\right) + A_5\left(\frac{P}{P_c}\right)^2 \qquad \text{(Eq. 5)}$$

$$T^{1} = A_6 + A_7\left(\frac{T}{T_c}\right) + A_8\left(\frac{T}{T_c}\right)^2 + A_9\left(\frac{P}{P_c}\right) + A_{10}\left(\frac{P}{P_c}\right)^2 \qquad \text{(Eq. 6)}$$

Table 1. Summary of the trimmed data used in the development of the generalized correlation



IUPAC Name	MW	Acentric Factor	Critical Temp.	Critical Pressure	Pressure	Temp. Range	Electrical Conductivity Range	Data Points	Reference
1-(2-hydroxyethyl)-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide	407.3	0.5172	1297.5	3307	101.325	283.15 - 353.15	0.1319 - 1.815	15	Liu et al. (2015)
1,2-dimethyl-3-propylimidazolium bis[(trifluoromethyl)sulfonyl]imide	419.36	0.32	1269.7	2746	100	293.15-323.15	0.196 - 0.687	7	Papovic et al. (2016)
1-butyl-3-methylimidazolium tetrafluoroborate	226.03	0.8877	643.2	2038	101.325	303 - 353	0.416 - 2.144	11	Iwasaki et al. (2017)

1-butyl-3-methylimidazolium tetrafluoroborate	226.03	0.8877	643.2	2038	101.325	298.15-333.15	0.36 - 1.516	8	Pandit et al. (2016)
1-butyl-3-methylimidazolium thiocyanate	197.30	0.4781	1047.4	1938	101.325	298.15-333.15	0.644 - 1.862	8	Pandit et al. (2016)
1-butyl-3-methylimidazolium tricyanomethane	229.29	0.9266	1185.1	2114	101.325	293.25 - 379.25	1.027 - 4.56	11	Zubeir et al. (2015)
1-butylpyridinium bis[(trifluoromethyl)sulfonyl]imide	416.35	0.2505	1229.1	2771	101.325	293-344	0.191 - 0.937	6	Dzida et al. (2019)
1-butylpyridinium bis[(trifluoromethyl)sulfonyl]imide	416.35	0.2505	1229.1	2771	101.325	278.15 - 438.15	0.1186 - 5.243	15	Nazet et al. (2017)
1-ethyl-2,3-dimethylimidazolium bis[(trifluoromethyl)sulfonyl]imide	405.33	0.2794	1258.9	2975	100	293.15-323.15	0.309 - 0.92	7	Papovic et al. (2016)
1-ethyl-3-methylimidazolium acetate	170.21	0.5889	807.1	2919	101	288.15 - 353.15	0.151 - 2.223	14	Zhang et al. (2017)
1-ethyl-3-methylimidazolium acetate	170.21	0.5889	807.1	2919	101	298.15 - 418.15	0.2776 - 6.917	13	Nazet et al. (2015)
1-ethyl-3-methylimidazolium acetate	170.21	0.5889	807.1	2919	101	298.15 - 323.15	0.2875 - 0.918	6	Oliveira et al. (2015)
1-ethyl-3-methylimidazolium methanesulfonate	206.26	0.3307	1026	4813	101.325	273.15 - 353.15	0.04134 - 1.994	19	Harris et al. (2016)
1-ethyl-3-methylimidazolium trifluoromethanesulfonate	260.23	0.3255	992.30	3584	101.325	273.15 - 353.15	0.346 - 3.287	13	Harris et al. (2016)
1-ethyl-3-methylimidazolium trifluoromethanesulfonate	260.23	0.3255	992.30	3584	101.325	297.65-304.65	0.81 - 1.14	5	Aranowski et al. (2016)
1-ethyl-3-methylimidazolium trifluoromethanesulfonate	260.23	0.3255	992.30	3584	101	288.15 - 333.15	0.605 - 2.236	3	Asenbauer et al. (2017)
1-ethylpyridinium bis[(trifluoromethyl)sulfonyl]imide	388.3	0.1671	1207.9	3275	101.325	303-343	0.528 - 1.335	5	Dzida et al. (2019)
1-octyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide	475.47	0.4811	1317.8	2098	101	273.15 - 468.15	0.0308 - 4.029	29	Nazet et al. (2015)
1-octyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide	475.47	0.4811	1317.8	2098	100	293.15 - 323.15	0.106 - 0.361	7	Papovic et al. (2016)
butylammonium formate	119.16	0.5182	521.1	3466	100	293.15 - 333.15	0.287 - 0.873	9	Wei et al. (2018)
propylammonium formate	105.14	0.4839	496.6	3919	101.325	293.15 - 333.15	0.31 - 1	9	Chhotaray et al. (2015)

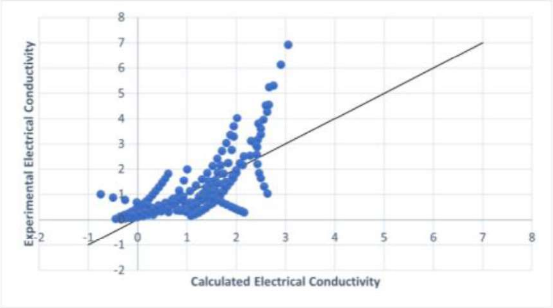


Figure 3. *Parity plot*

The residual, on the other hand, is shown in figures 4 and 5, plotted against the reduced pressure (Pr) and reduced temperature (Tr), respectively. Both figures show the patterned mathematical model is appropriate for the dataset. In addition, the plot shows that the residuals are not far from zero, indicating that the calculated electrical conductivity is close to the experimental electrical conductivity. It also shows that the model has both underprediction and overprediction of the data.

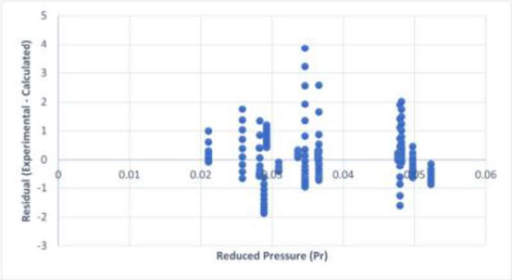


Figure 4. *Residual plotted against reduced pressure*

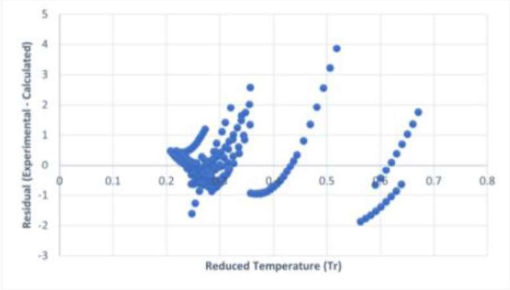


Figure 5. *Residual plotted against reduced temperature*

According to Van der Waals' Corresponding States Principle, substances behave alike at the same reduced states. Figure 6 shows the relationship between reduced pressure and the experimental data. Different colored lines connect the substances with the same reduced temperature. The graph for each reduced temperature follows the same pattern. However, as the reduced temperature decreases, the graph will have an inconsistent pattern compared to the graphs in Figure 6 and more complicated as shown on the graph of Tr = 0.26.

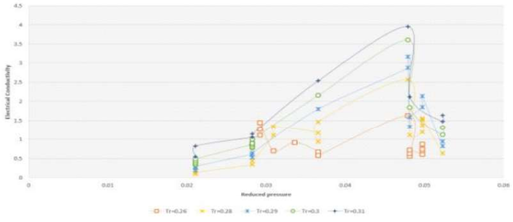


Figure 6. *Reduced pressure plotted against electrical conductivity*

4. CONCLUSIONS

The researchers have successfully created a model that can predict the electrical conductivity of pure ionic liquids. Using data trimming, the researchers have identified the most suitable data to be used in the study. Still, the unavailability of constants needed for the process significantly affected the number of the data point used in the study. Most of the calculated data from the model are close to their respective experimental values. However, there are some systems that the researchers have underestimated. Thus, further research should be conducted to have a more accurate prediction of the property. The model produced by this study can be used as a reference model for future studies that will be conducted. Manufacturers that would use this model as a basis for their research and innovation of their products should note some Ionic Liquid system that has been underestimated to be avoided since it is not accurate enough compared to other systems.

5. ACKNOWLEDGMENTS

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