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# A New Simple Model to Calculate the Heat Capacity of Pure Ionic Liquids

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In recent years, there is a great attention toward the ionic liquids due to their huge potential for separation and reaction technology. Also, the heat capacity of ionic liquids is a substantial parameter for conclusive process designs and engineering calculations. A database for the heat capacity of ionic liquids created by compiling experimental data in the literature covering a period from 1971 to 2016 is reported. In this work, a temperature-dependent equation to the heat capacity for 141 pure ionic liquids is proposed. A database containing 6961 experimental data was used to develop this model. Finally, a 7-parameter simple equation with the capability for predicting the heat capacity of ionic liquids is presented. The accuracy of the new model has been compared to the most precise models in the literature and the comparison indicates that the proposed method provides more accurate results than other models considered in this work. The average absolute percentage deviation from the new model is only 3.83%.

**Keywords:** Heat capacity, Ionic liquid, Correlation, NIST

## INTRODUCTION

Ionic liquids (IL) are a substance class that have attracted much attention since their insignificant vapor pressure and other properties make these substances interesting fluids for many processes and engineering designs. Options of investigations include solvents for using in absorption heat pumps [1], $CO_2$ removal from gas streams [2,3], and purification of biomaterials [4]. Ionic liquids have various characteristics of common salts which are normally having melting temperatures higher than 273 K [5-14].

The development of ionic liquids for special tasks is currently being followed by many researchers as much anion/cation combinations produce ionic liquids with a set of favorable properties. With rising the availability of experimental source data and their quality, the development of predictive models for ionic liquid properties and computer-aided molecular design (CAMD) of these substances becomes possible [15].

The constant pressure heat capacity (Cp) is specified as a derivative of the enthalpy as a function of temperature and constant pressure [16]. As *Cp* is linked to some thermodynamic properties like entropy, enthalpy, and Gibbs free energy, having good information about its behavior aids in the alternative study of other related properties. Also, Cp of both liquid and solid-state compounds is used to estimate heat transfer in many chemical operations and processes.

There are many methods available in the literature for the determination of the heat capacity of ionic liquids at constant pressure. Gardas and Coutinho [15] developed a 12-parameter model based on a second-order group additively method. They used a database comprising of 19 ionic liquids with 2,396 data points over a wide temperature range of (196.36-663.10 K). Soriano *et al.* [17] applied a similar approach to Gardas and Coutinho [15] by using anions and cations instead of group contribution methods. Their dataset had 32 ionic liquids and 3,149 data points with a temperature range of (188.06-663.10 K).

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Valderrama *et al*. [18] applied a new approach to estimate the heat capacity of ionic liquids which is called the mass connectivity index (MCI). Sattari *et al*. [19] developed a new model that combines a genetic function approximation (GFA) with a group-contribution (GC) method approaches for the estimation of liquid heat capacities at constant atmospheric pressure for ionic liquids. Muller and Albert [20] presented temperature-dependent contributions to the heat capacity for 32 anions and 39 cations with 2443 data points. Ahmadi *et al*. [21] proposed a temperature-dependent model with 13 constant parameters that uses molecular weight, temperature and the number of atoms (such as carbon, oxygen, hydrogen, nitrogen, *etc*.) in the structure of the ionic liquids as input with a database of approximately 128 different ionic liquids, consisting of 4822 experimental data. Farahani *et al*. [22] presented a temperature-dependent correlation based on molecular parameters to estimate the heat capacities of ionic liquids. A total data set of 2940 experimental data for 56 ionic liquids was used to develop this correlation. Zhang *et al*. [23] investigated the concept of the polarity coefficient for ionic liquids and developed a new model for estimating the difference of heat capacities between the vapor phase and the liquid phase of ionic [23]. Oster *et al*. [24] considered the predictive capabilities of existing models for thermal conductivity and heat capacity of pure ionic liquids, with further improvements based on more accurate investigated structure characterization (DFT) and reparameterization (group contribution methodology).

In this study, we present a simple correlation to cover a wide range of ionic liquids, for more developed applications than all exist in literature. A temperature-dependent correlation, based on the molecular parameters, including molecular weight and the number of elements such as hydrogen, carbon, nitrogen, oxygen, *etc*. in the structure of the ionic liquid, is proposed to predict the heat capacities of pure ionic liquids.

## PREDICTION OF HEAT CAPACITY OF IONIC LIQUIDS

In this study, we considered some of the well-known commonly used models that do not require specific coefficients for each substance but based on knowledge of some properties of the liquid-vapor equilibrium or molecular properties. In particular, we selected Ahmadi *et al*. [11], Muller-Albert [20], Farahani *et al*. [22] and Rostami *et al*. [25] models which are the newest most accurate correlations that are valid for the calculation of heat capacity. The correlations considered are presented below:

### Ahmadi *et al.* Method (AHRH)

Ahmadi *et al.* [21] in 2015 presented a 13-parameter correlation for the prediction of the heat capacity of ionic liquids. This is a temperature-dependent correlation that uses temperature, molecular weight and the number of atoms (such as carbon, oxygen, hydrogen, nitrogen, *etc*.) in the structure of the ionic liquids as input parameters. A databank of approximately 128 different ionic liquids, consisting of 4822 data points, was used to develop and validate this equation which includes a temperature ranges from 190-663 K,

$$C_p = a_1 T^{a_2} + a_3 \ln(T) + a_4 Mw^{a_5} + a_6 C_A + a_7 C_C + a_8 N + a_9 S + a_{10} O + a_{11}(F + Br + Cl) + a_{12} B + a_{13} \quad (1)$$

where T and Mw are the temperature (K) and molecular weight, respectively. The remaining parameters are all structure-related and defined as the number of atoms of: carbon in the anion (CA), carbon in the cation (CC), nitrogen (N), sulfur (S), oxygen (O), phosphorus (P), fluorine (F), bromine (Br), chlorine (Cl) and boron (B). The global constants of Ahmadi *et al*. correlation are presented in Table 1.

### Muller-Albert Method

Muller and Albert in 2014 [20] proposed a substance-dependent contribution to the heat capacity for 39 cations and 32 anions of ionic liquids. In this method, the NIST Standard Reference database 147 [26] was used to gather heat capacity data for ionic liquids. Muller-Albert correlation is presented as follows:

$$C_{P,ion} = A + BT + CT^2 \quad (2)$$

The parameters for Eq. (2) are given as Supporting

**Table 1.** The Constant Parameters of Ahmadi *et al*. Correlation

| Constant | Value |
|---|---|
| $a_1$ | 0.2808 |
| $a_2$ | 1.0854 |
| $a_3$ | -17.5066 |
| $a_4$ | 0.6593 |
| $a_5$ | 1.0793 |
| $a_6$ | 15.9932 |
| $a_7$ | 16.1292 |
| $a_8$ | -2.8956 |
| $a_9$ | -11.7667 |
| $a_{10}$ | -1.3729 |
| $a_{11}$ | -4.1977 |
| $a_{12}$ | 6.7438 |
| $a_{13}$ | -12.3990 |

Information in [20]. The heat capacity of the ionic liquids is derived by summing the heat capacity contributions of the cation and anion. If an ionic liquid contains more than one cation or anion, the heat capacity is calculated as:

$$C_{P,ionicliquid} = \sum_{i=cations} x_i c_{P,i} + \sum_{i=anions} x_j c_{P,j} \quad (3)$$

where $x_i$ and $x_j$ are the molar shares of the cation or anion on all cations or anions, respectively.

## Farahani *et al.* Model (FGMT)

Farahani *et al*. in 2013 [22] proposed a simple 5-term temperature-dependent correlation based on basic molecular parameters to predict heat capacities of ionic liquids. A total data set of 2940 experimental data belonging to ionic liquids were used to develop a general correlation. The model is presented as:

$$C_p = -122.16826 + 0.45794 \times T + 12.8395 \times N_{cation} - 56.85424 \times CH_3\text{-}R_{cation} + 19.25836 \times N_{anion} - 11.36109 \times nH_{anion} \quad (4)$$

where $C_p$ is the heat capacity of the ionic liquid, $T$ is the temperature in Kelvin, $N_{cation}$ and $N_{anion}$ are the number of atoms in cation and anion, respectively, $CH_3\text{-}R$ is the number of the methyl group in cation and $nH$ is the number of hydrogens in the anion.

## Rostami *et al.* Model (RHKHSR)

Rostami *et al.* [25] presented a hybrid group method of data handling (GMDH) to establish a model estimating the ionic liquid heat capacities. The database was taken from the NIST standard which includes the heat capacities of ionic liquids as a function of temperature and four structural parameters indicated in Eq. (5).

$$C_p = N_1 = -21.8587 + 0.0568103 \times (N-c) \times N_3 - 0.0669907 \times (N-c) \times N_2 + 0.0939589 \times (N-c)^2 - 0.0185935 \times N_2 \times N_3 + 0.00737194 \times (N_3)^2 + 1.08368 \times N_2 + 0.0114153 \times (N_2)^2 \quad (5)$$

$$N_2 = 14.1818 + 0.00640075 \times N_5 \times N_7 - 0.00420937 \times N_3 \times N_7 - 0.00112672 \times (N_7)^2 + 0.691339 \times N_5 + 0.00521464 \times N_3 \times N_5 - 0.00624998 \times (N_5)^2 + 0.266436 \times N_3 \quad (6)$$

$$N_3 = 55.6805 + 2.85758 \times (N\_a) + 0.0434574 \times (N-a) \times N_7 - 0.0332428 \times (N-a) \times N_4 - 0.217541 \times (N-a)^2 - 0.697195 \times N_7 + 0.00553497 \times N_4 \times N_7 - 0.00274183 \times (N_7)^2 + 1.46115 \times N_4 - 0.00275876 \times (N_4)^2 \quad (7)$$

$$N_4 = 157.505 - 0.267991 \times (T) - 0.346044 \times (T) \times (CH_3R_c) + 0.00162831 \times (T) \times N_7 + 0.000305718 \times (T)^2 + 136.314 \times (CH_3R_c) + 0.267234 \times (CH_3R_c) \times N_7 + 30.4506 \times (CH_3R_c)^2 + 0.000750235 \times (N_7)^2 \quad (8)$$

$$N_5 = -8.20417 + 6.53857 \times (N_a) - 0.70425 \times (N_a) \times (nH_a) - 0.0370242 \times (N_a) \times N_6 + 0.77614 \times (N_a)^2 - 7.08343 \times (nH_a) - 0.778415 \times (nH_a)^2 + 0.959609 \times N_6 + 0.000294705 \times (N_6)^2 \quad (9)$$

$$N_6 = -214.728 + 0.769769 \times (T) + 0.0112218 \times (T) \times (N_c) - 0.00076256 \times (T)^2 + 11.1858 \times (N_c) + 0.38969 \times (N_c) \times (N_a) - 0.0771166 \times (N_c)^2 + 13.8176 \times (N_a) - 0.334967 \times (N_a)^2 \quad (10)$$

$$N_7 = -88.0828 + 14.1091 \times (N_c) - 0.0968272 \times (N_c) \times (N_a) - 0.0163322 \times (N_c)^2 + 38.3889 \times (N_a) + 1.68527 \times (N_a) \times (nH_a) - 0.931272 \times (N_a)^2 - 40.5504 \times (nH_a) \quad (11)$$

## Data Preparation

The source data contains 6961 experimental data points for sonic speed of 141 ionic liquids with various pressure and temperatures. The experimental data covered a molecular weight, a wide range of temperatures and heat capacity [26]. A list of the ionic liquids making up the databank and the corresponded information for each liquid is presented in Table 2 and Table 2S. The properties of considered ionic liquids are shown in Table 3 and Table 3S.

# RESULTS AND DISCUSSION

## The Proposed Model for Heat Capacity

This study tried to find a rapid simple correlation to estimate the heat capacity of the ionic liquids based on experimental data with high accuracy by using temperature and molecular weight. There are some available experimental data in NIST Ionic Liquids Database [26] to allow the proposition of a model for heat capacity of the ionic liquids. After multiple regression analysis, a new equation (Eq. (12)) was suggested as follow:

$$C_p = a.T^b + c(T^{b+1} + Mw) + d(C_a + C_c) + e(N+S+P) + f.O + g(-F+Br+Cl+B) \quad (12)$$

where $T$ and $Mw$ are temperature ($K$) and molecular weight (g mol$^{-1}$), respectively. The remaining parameters are defined as the number of atoms of: carbon in the cation ($C_c$), carbon in the anion ($C_a$), bromine ($Br$), nitrogen ($N$), fluorine ($F$), oxygen ($O$), phosphorous ($P$), sulfur ($S$), chlorine ($Cl$) and boron ($B$). The constant parameters of Eq. (2) are presented in Table 3 and Table 3S.

To present a more general and accurate atomic correlation than the previous models, a wide set of commonly used ionic liquids has been considered in this work. The number of carbon atoms in the anion and cation, as well as other atoms consisting of sulfur, nitrogen, oxygen, phosphorus, bromine, fluorine, boron and chlorine, were found to be the most effective parameters to identify the behavior of ionic liquids. The functionality for each of the mentioned atoms, similar to previous models, was considered to be a simple additive term which includes the number of a particular atom in the structure multiplied by a constant parameter that is optimized. In the present method, by considering selected atoms as input parameters to the correlation and including mathematical temperature functionality likewise, various regression analysis was carried out on the 6420 training data of the 132 ionic liquids (indicated in the last column of Table 3 and Table 3S) and

**Table 2.** Name and Structure of Ionic Liquids Considered

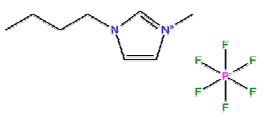
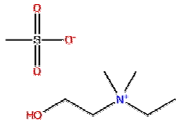
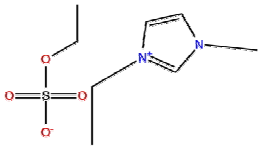
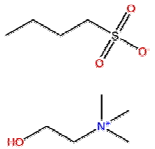
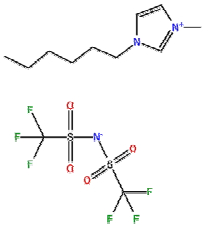
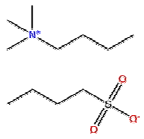
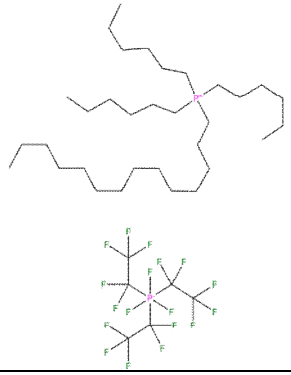
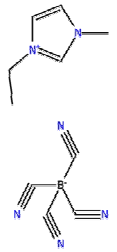
| No | Name | Formula | Structure | No | Name | Formula | Structure |
|---|---|---|---|---|---|---|---|
| 1 | 1-Butyl-3-methylimidazolium hexafluorophosphate | $C_8H_{15}F_6N_2P$ |  | 72 | N-ethyl-2-hydroxy-N,N-dimethylethanaminium methanesulfonate | $C_7H_{19}NO_4S$ |  |
| 2 | 1-Ethyl-3-methylimidazolium ethyl sulfate | $C_8H_{16}N_2O_4S$ |  | 73 | 2-Hydroxy-N,N,N-trimethyl-ethanaminium 1-butanesulfonate | $C_9H_{23}NO_4S$ |  |
| 3 | 1-Hexyl-3-methylimidazolium bis[(trifluoromethyl) sulfonyl]imide | $C_{12}H_{19}F_6N_3O_4S_2$ |  | 74 | N,N,N-trimethyl-1-butanaminium 1-butanesulfonate | $C_{11}H_{27}NO_3S$ |  |
| 4 | Trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl) trifluorophosphate | $C_{38}H_{68}F_{18}P_2$ |  | 75 | 1-Ethyl-3-methylimidazolium tetracyanoborate | $C_{10}H_{11}BN_6$ |  |

**Table 2.** Continued

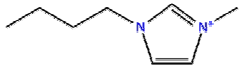
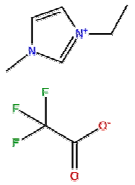
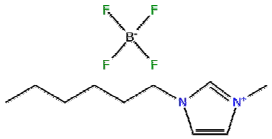
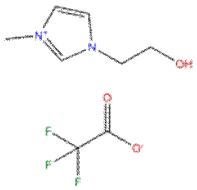
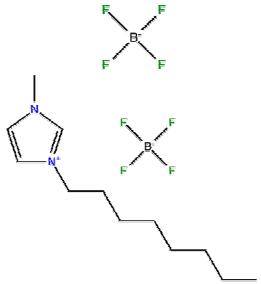
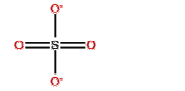
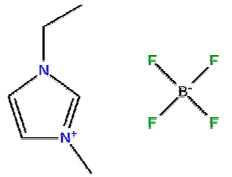
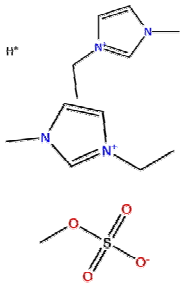
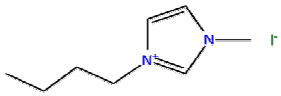
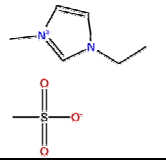
| | | | | | | |
|---|---|---|---|---|---|---|
| 5 | 1-Butyl-3-methylimidazolium tetrafluoroborate | $C_8H_{15}BF_4N_2$ |  | 76 | 1H-imidazolium, 1-ethyl-3-methyl-, salt with trifluoroacetic acid (1:1) | $C_8H_{11}F_3N_2O_2$ |  |
| 6 | 1-Hexyl-3-methylimidazolium tetrafluoroborate | $C_{10}H_{19}BF_4N_2$ |  | 77 | 1-(2-Hydroxyethyl)-3-methyl-1H-imidazolium 2,2,2-trifluoroacetate | $C_8H_{11}F_3N_2O_3$ |  |
| 7 | 1-Methyl-3-octylimidazolium tetrafluoroborate | $C_{12}H_{23}BF_4N_2$ |  | 78 | 1-Ethyl-3-methylimidazolium hydrogen sulfate | $C_6H_{12}N_2O_4S$ |  |
| 8 | 1-Ethyl-3-methylimidazolium tetrafluoroborate | $C_6H_{11}BF_4N_2$ |  | 79 | 1-Ethyl-3-methylimidazolium methylsulfate | $C_7H_{14}N_2O_4S$ |  |
| 9 | 1-Butyl-3-methylimidazolium iodide | $C_8H_{15}IN_2$ |  | 80 | 1-Ethyl-3-methylimidazolium methanesulfonate | $C_7H_{14}N_2O_3S$ |  |

**Table 3.** Name and Structure of Ionic Liquids

| No. | Name | Formula | No. Data | Mw | $T$ range | $C_p$ range | Use as |
|---|---|---|---|---|---|---|---|
| 1 | 1-Butyl-3-methylimidazolium hexafluorophosphate | $C_8H_{15}F_6N_2P$ | 1633 | 284.18 | 283.15-524.87 | 367.3-510 | Training |
| 2 | 1-Hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide | $C_{12}H_{19}F_6N_3O_4S_2$ | 502 | 447.42 | 188.06-425.15 | 572-739 | Training |
| 3 | 1-Ethyl-3-methylimidazolium ethyl sulfate | $C_8H_{16}N_2O_4S$ | 450 | 236.29 | 187.36-377.2 | 347-570 | Training |
| 4 | 1-Butyl-3-methylimidazolium tetrafluoroborate | $C_8H_{15}BF_4N_2$ | 374 | 226.02 | 181.25-423.15 | 276.1-520 | Validation |
| 5 | 1-Methyl-3-propylimidazolium bromide | $C_7H_{13}BrN_2$ | 261 | 205.1 | 212.2-370 | 256.1-307 | Training |
| 6 | 1-Methyl-3-octylimidazolium tetrafluoroborate | $C_{12}H_{23}BF_4N_2$ | 246 | 282.13 | 192.85-370 | 463.2-544.2 | Training |
| 7 | 1-Ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide | $C_8H_{11}F_6N_3O_4S_2$ | 178 | 391.31 | 256.91-463.15 | 456-559 | Training |
| 8 | 1-Butyl-3-methylimidazolium dicyanamide | $C_{10}H_{15}N_5$ | 156 | 205.26 | 235-372.2 | 355.9-413.6 | Training |
| 9 | 1-Butyl-3-methylimidazolium trifluoromethanesulfonate | $C_9H_{15}F_3N_2O_3S$ | 152 | 288.29 | 290.98-425.15 | 417.2-506 | Training |
| 10 | Trihexyl(tetradecyl)phosphonium bis[(trifluoromethyl)sulfonyl]imide | $C_{34}H_{68}F_6NO_4PS_2$ | 150 | 764 | 293-463.15 | 1360-1570 | Training |
| 11 | Trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate | $C_{38}H_{68}F_{18}P_2$ | 143 | 928.87 | 338.15-513.15 | 1540-1810 | Training |
| 12 | 1-Butyl-3-methylimidazolium iodide | $C_8H_{15}IN_2$ | 134 | 266.12 | 209.86-370 | 285.8-336.9 | Training |
| 13 | 1-Butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide | $C_{10}H_{15}F_6N_3O_4S_2$ | 123 | 419.36 | 190-363.18 | 524-602.1 | Training |
| 14 | 1-Hexyl-3-methylimidazolium trifluoromethanesulfonate | $C_{11}H_{19}F_3N_2O_3S$ | 112 | 316.34 | 283.15-425.15 | 484-589 | Training |

**Table 3.** Continued

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 15 | 2-Hydroxy-N-methylethanaminium propionate | $C_6H_{15}NO_3$ | 111 | 149.19 | 287.15-326.15 | 323-336 | Training |
| 16 | 2-Hydroxy-N-methylethanaminium pentanoate | $C_8H_{19}NO_3$ | 107 | 177.24 | 283.15-333.15 | 385-421 | Training |
| 17 | N-methyl-2-hydroxyethylammonium butanoate | $C_7H_{17}NO_3$ | 92 | 163.21 | 286.15-336.15 | 357-385 | Training |
| 18 | 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate | $C_7H_{11}F_3N_2O_3S$ | 76 | 260.23 | 303.2-425.15 | 379-425 | Training |
| 19 | 4-(Dimethylamino)-1-hexyl-pyridinium 1,1,1-trifluoro-N-[(trifluoromethyl)sulfonyl]methanesulfonamide | $C_{15}H_{23}F_6N_3O_4S_2$ | 73 | 487.48 | 298-425.15 | 663-825 | Training |
| 20 | n-butyl-4-(n',n'-dimethylammonium)pyridinium bis(trifluoromethylsulfonyl)imid | $C_{13}H_{19}F_6N_3O_4S_2$ | 73 | 459.43 | 298-425.15 | 611-739 | Training |
| 21 | 1-Octyl-3-methylimidazolium trifluoromethanesulfonate | $C_{13}H_{23}F_3N_2O_3S$ | 64 | 344.39 | 313.17-425.15 | 588-680 | Training |
| 22 | n-ethyl-4-(n',n'-dimethylammonium)pyridinium bis(trifluoromethylsulfonyl)imide | $C_{11}H_{15}F_6N_3O_4S_2$ | 64 | 431.37 | 313.12-425.15 | 590-659 | Training |
| 23 | 1-Butylpyridinium tetrafluoroborate | $C_9H_{14}BF_4N$ | 63 | 223.02 | 284.33-390 | 377.19-428.5 | Training |
| 24 | Tetradecyl(trihexyl)phosphonium dicyanamide | $C_{34}H_{68}N_3P$ | 63 | 549.9 | 313.15-413.15 | 1060-1240 | Training |
| 25 | 1-Butyl-1-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide | $C_{11}H_{20}F_6N_2O_4S_2$ | 61 | 422.41 | 237.44-347.44 | 546.8-622.4 | Validation |
| 26 | 1-Butylpyridinium bis[(trifluoromethyl)sulfonyl]imide | $C_{11}H_{14}F_6N_2O_4S_2$ | 60 | 416.36 | 323.18-425.15 | 587-645 | Training |
| 27 | 3-Methyl-1-propyl-1H-imidazolium (S)-2-amino-4-carboxybutanoate | $C_{12}H_{21}N_3O_4$ | 58 | 271.31 | 244.25-357.7 | 471-568.1 | Training |
| 28 | 1-Methyl-1-propylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide | $C_{10}H_{18}F_6N_2O_4S_2$ | 57 | 408.38 | 283.15-358.15 | 541-606 | Training |

the resulting optimized equation for heat capacity, in (J $mol^{-1}$ $K^{-1}$), is suggested. To compare the accuracy of the presented empirical model, the calculated heat capacity of training data versus corresponded values of the data bank has been presented in Fig. 1.

To estimate the applicability of the presented correlation in the prediction of heat capacity of data has not participated in training procedure, the proposed equation was verified using the remaining 541 data points, from 11 different ionic liquids (indicated in the last column of Table 3 and Table 3S). The heat capacities predicted with the correlation in this manner were compared to the corresponding experimental data. The resulting average absolute relative deviation (AARD%) is presented in Fig. 2.

The criteria for comparisons are AARD%, ARD% and RMSD which calculated as follows:

$$AARD\% = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{P_{i,\exp} - P_{i,calc}}{P_{i,\exp}}\right| \times 100 \quad (13)$$

$$ARD\% = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{P_{i,\exp} - P_{i,calc}}{P_{i,\exp}}\right) \times 100 \quad (14)$$

$$RMSD = \frac{1}{N}\sqrt{\sum_{i=1}^{N}\left(\frac{P_{i,\exp} - P_{i,calc}}{P_{i,\exp}}\right)^2} \times 100 \quad (15)$$

In Table 4 and Table 4S, the AARD% of ionic liquids calculated from the proposed and other models for each substance along with the values given by data bank were presented.

It is worth mentioning that the Muller-Albert correlation is only applicable to 59 ionic liquids among 141 liquids considered in this study. Because of the high average absolute relative deviation of the Muller-Albert correlation (AARD > 50%), the results of the Muller-Albert model were eliminated in comparisons accomplished in this study.

To best comparison of this study equation *versus* AHRH, FGMT and RHKHSR models, all considered data onto ionic liquids from databank were used and statistical parameters of four considered models with a new set of data are presented in Figs. 3-5.

Figures 3-5 present the statistical parameters including average absolute percentage relative deviation percentages (AARD% in Fig. 3), average relative deviation, (ARD% in Fig. 4), and root mean square deviation (RMSD in Fig. 5) of four considered models for all 6961 experimental data onto 141 ionic liquids.

Figure 6 shows the cumulative frequency of the proposed model and literature three models for all experimental data *versus* average absolute relative deviations of all ionic liquids considered.

Cumulative frequency analysis is the analysis of the frequency of the occurrence of values of a phenomenon less than a reference value. Cumulative frequency analysis is performed to obtain insight into how often a certain phenomenon (feature) is below a certain value. This may help in describing a situation in which the phenomenon is involved, or in planning interventions. This analysis can make a good comparison between all models for all AARD% values. Each curve with more tendencies towards the top left corner of the plot square has more accuracy than the lower curves.

Figure 5 also shows the accuracy of two considered methods in prediction of heat capacity of more than 141 pure ionic liquids. As shown in Fig. 3, the new equation is more accurate than the other newest model in heat capacity prediction.

The new method has successfully predicted 56% of all data with AARD% less than 2, and 96% of the data with AARD% less than 10. Only 0.6% of the vapor pressure data was predicted with AARD% of more than 15 by the new method. The AHRH equation, the second accurate method, predicted 46% of the data with AARD% less than 2, and 82% of the data with AARD% less than 10.

It showed that the new method has successfully predicted 64% of all data with AARD% less than 2, and 87% of the data with AARD% less than 5. Only 2% of the vapor pressure data was predicted with AARD% of more than 10 by the new method. The Muller *et al.* equation, the second accurate method, predicted 51% of the data with AARD% less than 2, and 78% of the data with AARD% less than 5. Hence the superiority of this new method over the other corresponding state has been verified for all data existed in the data bank.

## CONCLUSIONS

Different methods can be used to calculate the heat capacities of ionic liquids such as empirical equations,

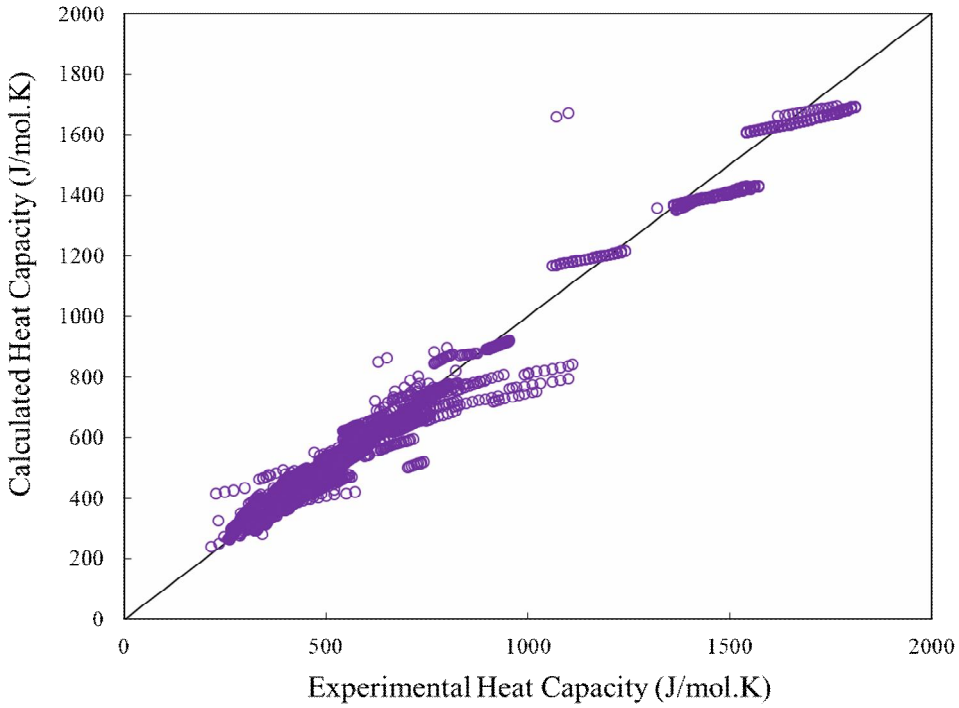



**Fig. 1.** Accuracy of the presented model *versus* training data.

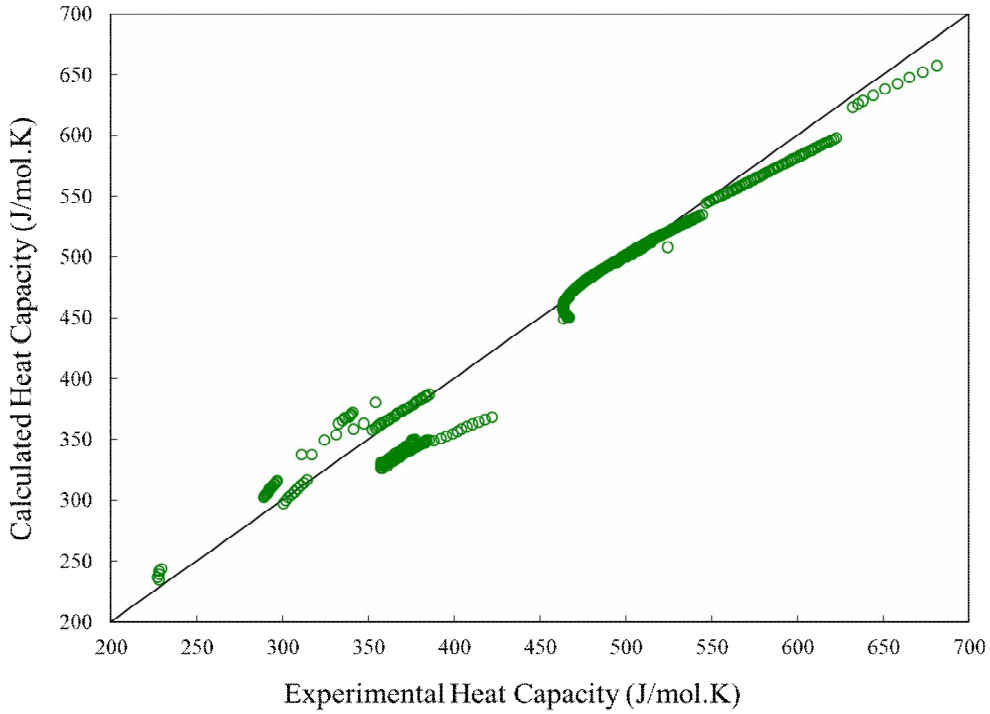



**Fig. 2.** Accuracy of the presented model *versus* validation data.

**Table 4.** Comparison the AARD% Values of the Presented Model with Literature Model

| No. | Name | Formula | No of Data | AHRH | FGMT | RHKHSR | This study |
|---|---|---|---|---|---|---|---|
| 1 | 1-Butyl-3-methylimidazolium hexafluorophosphate | $C_8H_{15}F_6N_2P$ | 1633 | 1.18 | 1.19 | 14.68 | 1.07 |
| 2 | 1-Hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide | $C_{12}H_{19}F_6N_3O_4S_2$ | 502 | 2.46 | 7.88 | 10.67 | 2.54 |
| 3 | 1-Ethyl-3-methylimidazolium ethyl sulfate | $C_8H_{16}N_2O_4S$ | 450 | 5.39 | 19.05 | 16.01 | 2.27 |
| 4 | 1-Butyl-3-methylimidazolium tetrafluoroborate | $C_8H_{15}BF_4N_2$ | 374 | 2.83 | 15.69 | 36.26 | 2.94 |
| 5 | 1-Methyl-3-propylimidazolium bromide | $C_7H_{13}BrN_2$ | 261 | 17.77 | 29.42 | 55.89 | 7.51 |
| 6 | 1-Methyl-3-octylimidazolium tetrafluoroborate | $C_{12}H_{23}BF_4N_2$ | 246 | 1.38 | 5.73 | 28.71 | 0.79 |
| 7 | 1-Ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide | $C_8H_{11}F_6N_3O_4S_2$ | 178 | 3.05 | 11.97 | 11.87 | 3.22 |
| 8 | 1-Butyl-3-methylimidazolium dicyanamide | $C_{10}H_{15}N_5$ | 156 | 0.93 | 14.94 | 30.79 | 1.53 |
| 9 | 1-Butyl-3-methylimidazolium trifluoromethanesulfonate | $C_9H_{15}F_3N_2O_3S$ | 152 | 2.55 | 14.00 | 16.35 | 3.43 |
| 10 | Trihexyl(tetradecyl)phosphonium bis[(trifluoromethyl)sulfonyl]imide | $C_{34}H_{68}F_6NO_4PS_2$ | 150 | 3.57 | 3.33 | 15.78 | 4.18 |
| 11 | Trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate | $C_{38}H_{68}F_{18}P_2$ | 143 | 3.12 | 4.25 | 14.21 | 3.40 |
| 12 | 1-Butyl-3-methylimidazolium iodide | $C_8H_{15}IN_2$ | 134 | 35.27 | 28.07 | 51.76 | 17.56 |
| 13 | 1-Butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide | $C_{10}H_{15}F_6N_3O_4S_2$ | 123 | 7.10 | 8.26 | 13.68 | 3.50 |
| 14 | 1-Hexyl-3-methylimidazolium trifluoromethanesulfonate | $C_{11}H_{19}F_3N_2O_3S$ | 112 | 4.47 | 12.34 | 13.83 | 1.76 |
| 15 | 2-Hydroxy-N-methylethanaminium propionate | $C_6H_{15}NO_3$ | 111 | 20.68 | 12.57 | 7.28 | 8.34 |
| 16 | 2-Hydroxy-N-methylethanaminium pentanoate | $C_8H_{19}NO_3$ | 107 | 19.55 | 10.86 | 3.40 | 8.64 |
| 17 | N-methyl-2-hydroxyethylammonium butanoate | $C_7H_{17}NO_3$ | 92 | 19.68 | 11.28 | 4.75 | 8.12 |
| 18 | 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate | $C_7H_{11}F_3N_2O_3S$ | 76 | 1.18 | 18.30 | 15.39 | 4.26 |
| 19 | 4-(Dimethylamino)-1-hexyl-pyridinium 1,1,1-trifluoro-N-[(trifluoromethyl)sulfonyl]methanesulfonamide | $C_{15}H_{23}F_6N_3O_4S_2$ | 73 | 2.97 | 14.87 | 7.80 | 3.09 |
| 20 | n-butyl-4-(n',n'-dimethylammonium)pyridinium bis(trifluoromethylsulfonyl)imid | $C_{13}H_{19}F_6N_3O_4S_2$ | 73 | 2.45 | 17.59 | 6.64 | 2.63 |

**Table 4.** Continued

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 21 | 1-Octyl-3-methylimidazolium trifluoromethanesulfonate | $C_{13}H_{23}F_3N_2O_3S$ | 64 | 5.77 | 10.44 | 13.59 | 1.95 |
| 22 | n-ethyl-4-(n',n'-dimethylammonium)pyridinium bis(trifluoromethylsulfonyl)imide | $C_{11}H_{15}F_6N_3O_4S_2$ | 64 | 1.44 | 20.12 | 4.92 | 1.53 |
| 23 | Tetradecyl(trihexyl)phosphonium dicyanamide | $C_{34}H_{68}N_3P$ | 63 | 3.90 | 5.05 | 28.05 | 4.05 |
| 24 | 1-Butylpyridinium tetrafluoroborate | $C_9H_{14}BF_4N$ | 63 | 0.69 | 5.50 | 10.55 | 4.44 |
| 25 | 1-Butyl-1-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide | $C_{11}H_{20}F_6N_2O_4S_2$ | 61 | 5.54 | 7.75 | 15.61 | 2.14 |
| 26 | 1-Butylpyridinium bis[(trifluoromethyl)sulfonyl]imide | $C_{11}H_{14}F_6N_2O_4S_2$ | 60 | 0.81 | 4.70 | 6.10 | 1.69 |
| 27 | 3-Methyl-1-propyl-1H-imidazolium (S)-2-amino-4-carboxybutanoate | $C_{12}H_{21}N_3O_4$ | 58 | 6.68 | 14.93 | 5.03 | 2.24 |
| 28 | 1-Methyl-1-propylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide | $C_{10}H_{18}F_6N_2O_4S_2$ | 57 | 2.31 | 4.58 | 18.08 | 4.59 |
| 29 | 1-Hexyl-3-methylimidazolium hexafluorophosphate | $C_{10}H_{19}F_6N_2P$ | 51 | 11.86 | 14.64 | 27.26 | 11.99 |
| 30 | Tributylmethylphosphonium methylsulphate | $C_{14}H_{33}O_4PS$ | 50 | 12.78 | 24.45 | 11.28 | 9.23 |
| 31 | 1-Tetradecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide | $C_{20}H_{35}F_6N_3O_4S_2$ | 50 | 1.31 | 0.98 | 11.74 | 1.75 |
| 32 | N-(2-hydroxyethyl)-N,N-dimethylpropanaminium bromide | $C_7H_{18}BrNO$ | 48 | 2.62 | 31.76 | 2.87 | 0.59 |
| 33 | Butyltrimethylammonium bis(trifluoromethylsulfonyl)imide | $C_9H_{18}F_6N_2O_4S_2$ | 48 | 5.98 | 26.68 | 8.60 | 5.43 |
| 34 | 1-Butyl-3-methylimidazolium octyl sulfate | $C_{16}H_{32}N_2O_4S$ | 46 | 4.86 | 7.33 | 4.03 | 1.53 |
| 35 | 1-Ethyl-3-methylimidazolium tetrafluoroborate | $C_6H_{11}BF_4N_2$ | 44 | 0.79 | 20.26 | 36.24 | 0.82 |
| 36 | 1-Butyl-3-methylpyridinium 1,1,1-trifluoro-N-[(trifluoromethyl)sulfonyl]methanesulfonamide | $C_{12}H_{16}F_6N_2O_4S_2$ | 43 | 10.19 | 4.01 | 18.41 | 11.72 |
| 37 | 1-Methyl-3-propylimidazolium bis[(trifluoromethyl)sulfonyl]imide | $C_9H_{13}F_6N_3O_4S_2$ | 42 | 8.33 | 4.38 | 20.89 | 7.10 |
| 38 | 1-Ethyl-3-methyl-1H-imidazolium tricyanomethanide | $C_{10}H_{11}N_5$ | 40 | 2.77 | 21.63 | 18.41 | 2.49 |
| 39 | 1-Hexyl-3-methylimidazolium tetrafluoroborate | $C_{10}H_{19}BF_4N_2$ | 33 | 0.47 | 7.92 | 27.22 | 1.43 |
| 40 | 1-Octyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide | $C_{14}H_{23}F_6N_3O_4S_2$ | 33 | 4.69 | 8.83 | 9.09 | 5.17 |

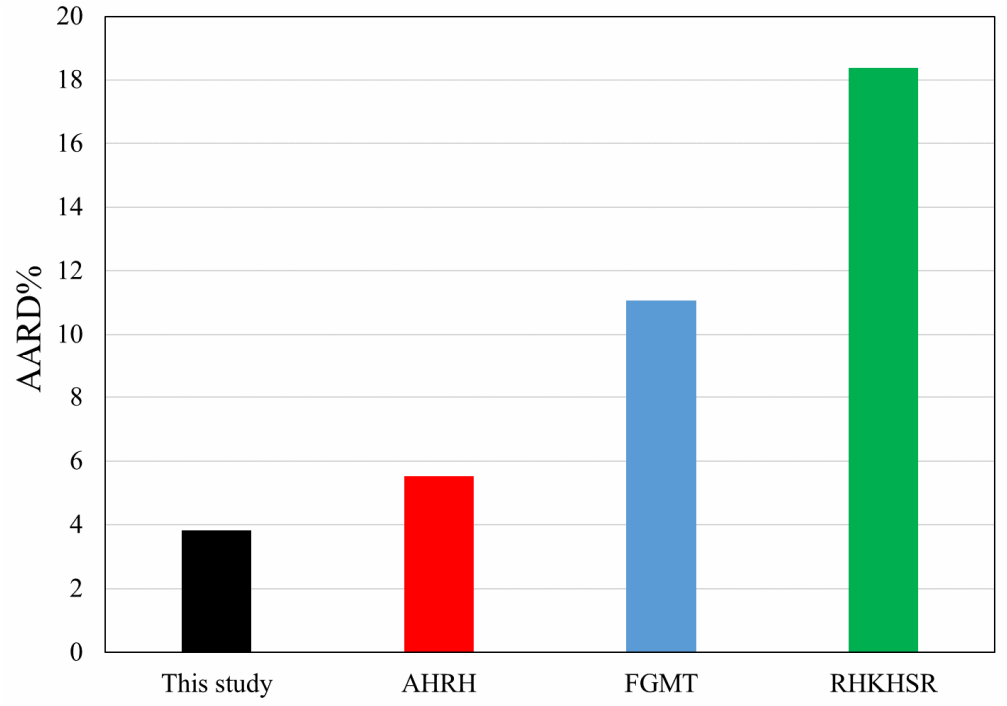



**Fig. 3.** AARD of four considered models.

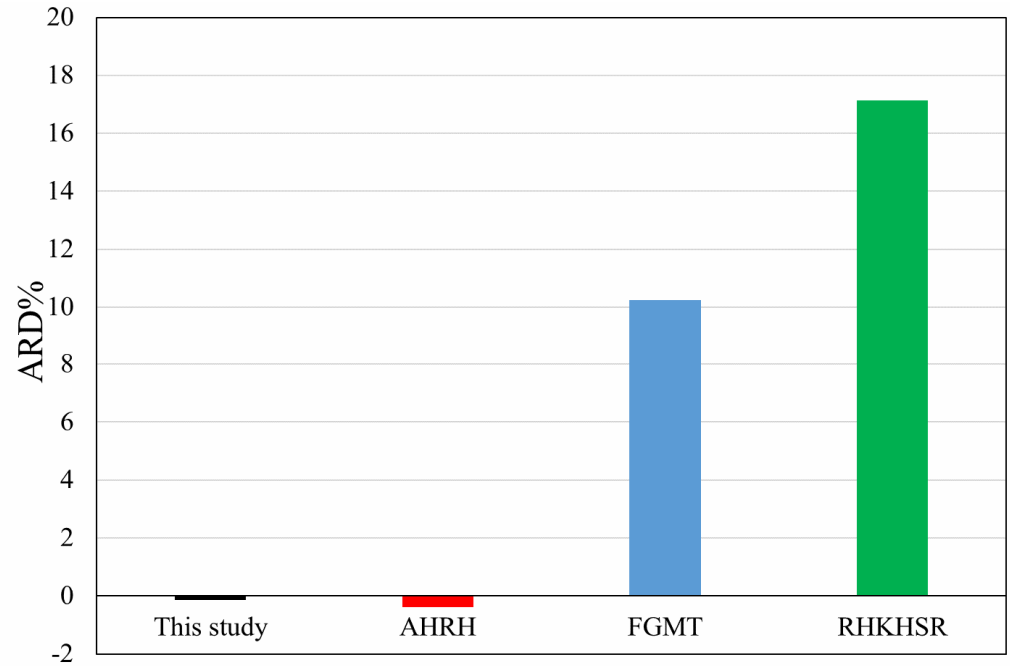



**Fig. 4.** ARD of four considered models.

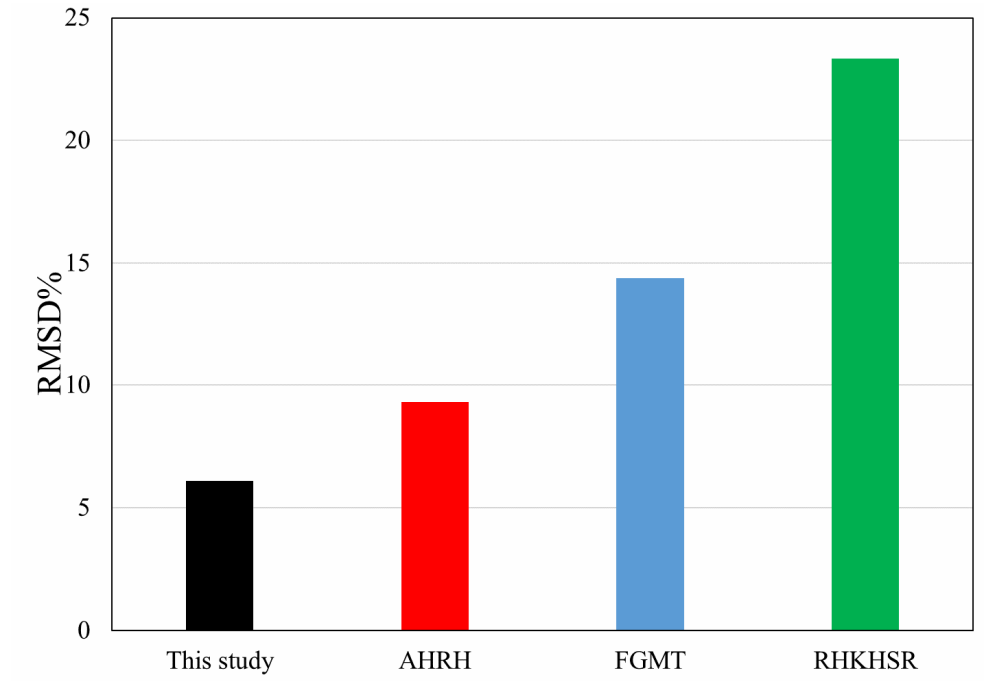



**Fig. 5.** RMSD of four considered models.

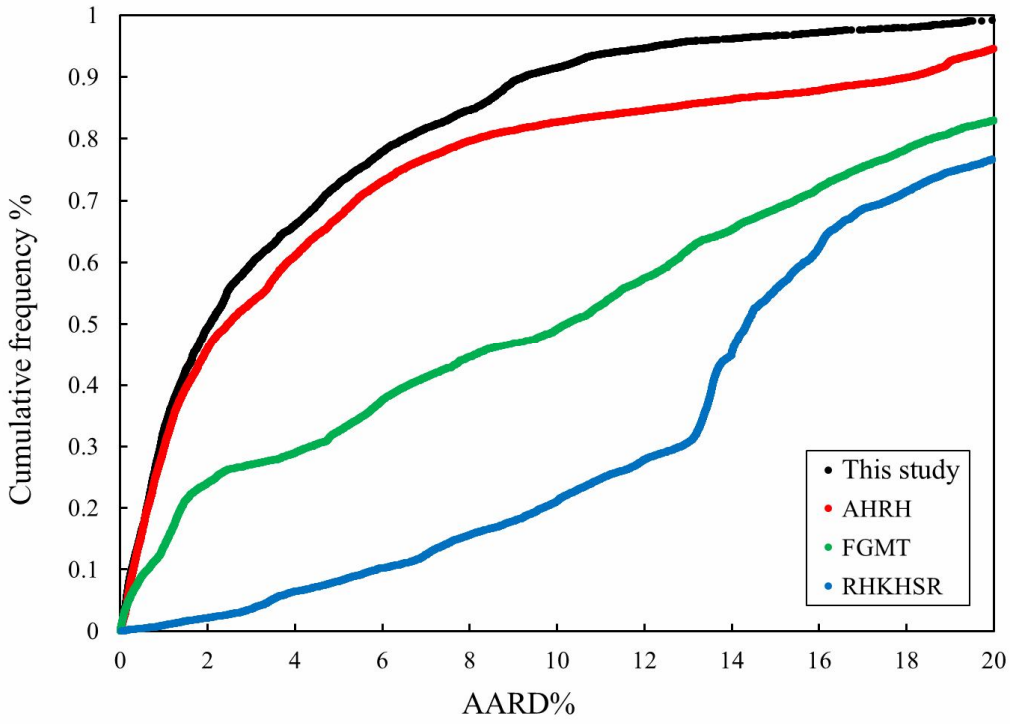



**Fig. 5.** AARD% of two methods in calculating heat capacity as a function of cumulative frequency.

group contributions, artificial neural networks, etc. In this study, two empirical literature methods are compared and evaluated. The AHRH model with 13 constant parameters, and FGMT substance-independent correlation with 6 parameters, and RHKHSR model with 61 constant parameters are considered. These three models generally give a good prediction of accuracy relative to other literature models which are not discussed in this study. A new 7-constant non-linear predictive model was recommended to estimate the heat capacity of pure ionic liquids more accurate than literature commonly used models. The presented equation is a function of temperature, molecular weight and the number of elements such as hydrogen, carbon, nitrogen, oxygen, *etc*. in cation and anions. To validate the proposed model, the heat capacity of 141 pure ionic liquids with 6961 data points has been examined and an overall average absolute percentage deviation of 3.83% is achieved.

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