Regular Article

An Accurate Empirical Correlation to Estimate Sonic speed of Ionic Liquids

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(Received 3 February 2015, Accepted 16 March 2015)

In recent years, there has been a great deal of attention paid by researchers in investigating ionic liquids (ILs) mainly due to the tremendous potential of them in reaction and separation technology. Sonic speed is an important thermodynamic property of ionic liquids (ILs) which has been always chosen as a source to determine other properties. A database for the sonic speed of pure ILs created by collecting experimental data from literature covering the period from 2005 to 2013 is presented. In this study, based on sonic speed experimental data, for the first time the relationship between boiling temperature, reduced temperature and pressure for 2198 data of 29 ionic liquids covering wide ranges of temperature, pressure, and sonic speed has been examined. In results, a 6-parameter model with ability for predicting the sonic speed of ionic liquids is presented. The obtained model has an average absolute relative deviation (AARD%) of 1.30%, a determination coefficient (R^2) of 0.987, and a root mean square error (RSMD) of 1.85.

INTRODUCTION

Ionic liquids (ILs), as possible replacements for volatile organic solvents, have been widely investigated due to their distinctive properties such as negligible vapor pressure, large liquidus range, high thermal stability, high ionic conductivity, and large electrochemical window. Knowledge of the physical and chemical properties of ILs is essentially important to optimize the use of ILs and design the desirable ILs. The sonic speed, *u*, is an important thermodynamic property that can be experimentally determined with great precision over a broad range of temperature and pressure, and it can be related to the other thermodynamic properties such as density, heat capacity, thermal conductivity, and isentropic and isothermal compressibility, which are essential for the accurate design and optimization of several industrial processes [1,2]. Experimental data for sonic speed of ionic liquids is very scarce and limited to imidazolium based ionic liquids. When developing ionic liquids for a given purpose, if

experimentally measured sonic speed data are not available, theoretical or empirical methods must be used to establish if the sonic speed is within acceptable limiting values defined in the design specifications. For this purpose prediction methods for sonic speed of ionic liquids are required [3].

While much work has been devoted to the wide range of applications of ILs, the basic understanding and study of their structure-property relationships is of equivalent importance but has lagged behind. Very few works have systematically studied the qualitative and/or quantitative relationships between the structures of ILs and their fundamental properties, such as melting point, viscosity, density, surface tension, thermal and electrochemical stability, solvent properties, and sonic speed. To better understand the nature of ionic liquids and rationally expand their applications, knowledge of their physical properties is required [3].

Given the huge potentials of ILs, experimental data of sonic speed for all ILs are still very insufficient. Therefore, it is of a great importance to develop a method for estimating the sonic speed of ILs with a wide range of applicability and favorable accuracy. The reports on the

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prediction of the sonic speed are still scarce. Several papers [4-6] tried to obtain the calculated values of the sonic speed for ILs by theoretical and empirical formulas, such as Auerbach's equation. Auerbach's equation [7] is a well-known empirical relation between the sonic speed, surface tension, and density of liquids.

$$u = \left(\frac{\sigma}{6.33 \times 10^{-10} \rho} \right)^{a} \qquad (1)$$

Where a equals 2/3, u is the sonic speed in m/s, σ is the surface tension in N/m, and ρ is the density in kg/m^3.

The aim of this study is to develop a new empirical correlation to predict the sonic speed of various classes of ILs with high accuracy, depending on boiling temperature, reduced temperature and pressure for the first time. The source of sonic speed data used in this study is experimental data from literatures [8-23].

By investigating the modeling approaches, the proposed method in this study can be regarded as an innovative and original equation to predict sonic speed for 29 commonly used ionic liquids.

METHODOLOGY

Data Preparation

The database contains 2198 experimental data points for sonic speed of 29 ionic liquids with various pressures. The experimental data covered a wide range of temperatures, pressure, and sonic speed. The names and structures of the considered ionic liquids are shown in Table 1.
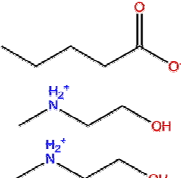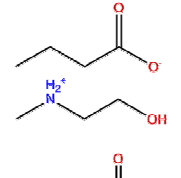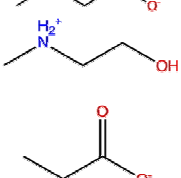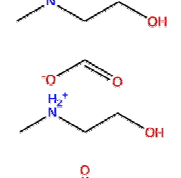
Table 1. Name and Structure of Ionic Liquids
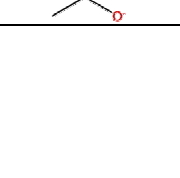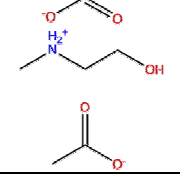
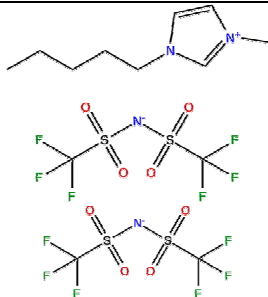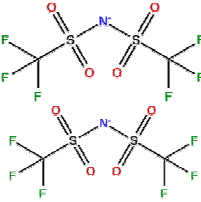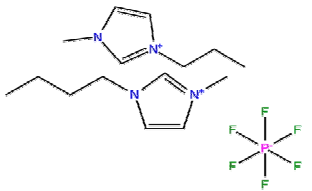| No.	Name	Formula	Structure
1	2-Hydroxy-N-methylethanaminium pentanoate	$C_8H_{19}NO_3$	
2	2-Hydroxy-N-methylethanaminium isobutyrate	$C_7H_{17}NO_3$	
3	N-Methyl-2-hydroxyethylammonium butanoate	$C_7H_{17}NO_3$	
4	2-Hydroxy-N-methylethanaminium propionate	$C_6H_{15}NO_3$	
5	2-Hydroxy-N-methylethanaminium formate	$C_4H_{11}NO_3$	
6	N-Methyl-2-hydroxyethylammonium acetate	$C_5H_{13}NO_3$	

Table 1. Continued
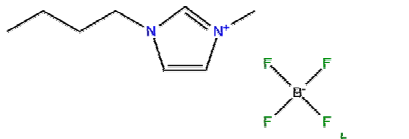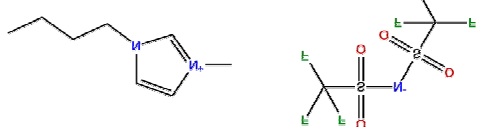
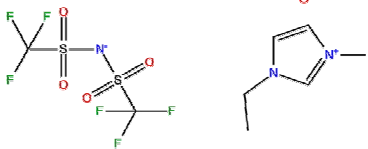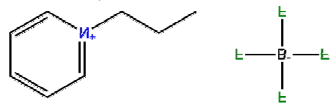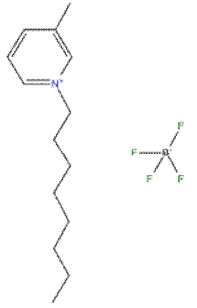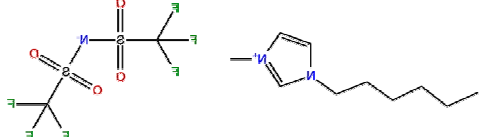|			
7	1-Pentyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide	$C_{11}H_{17}F_6N_3O_4S_2$	
8	1-Methyl-3-propylimidazolium bis[(trifluoromethyl)sulfonyl]imide	$C_9H_{13}F_6N_3O_4S_2$	
9	1-Butyl-3-methylimidazolium hexafluorophosphate	$C_8H_{15}F_6N_2P$	
10	1-Butyl-3-methylimidazolium octyl sulfate	$C_{16}H_{32}N_2O_4S$	
11	1-Butyl-3-methylimidazolium tetrafluoroborate	$C_8H_{15}BF_4N_2$	
12	1-Butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide	$C_{10}H_{15}F_6N_3O_4S_2$	
13	1-Ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide	$C_8H_{11}F_6N_3O_4S_2$	
14	1-Propylpyridinium tetrafluoroborate	$C_8H_{12}BF_4N$	
15	N-Octyl-3-methylpyridinium tetrafluoroborate	$C_{14}H_{24}BF_4N$	
16	1-Hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide	$C_{12}H_{19}F_6N_3O_4S_2$	

Table 1. Continued
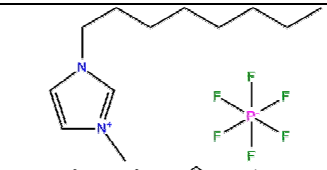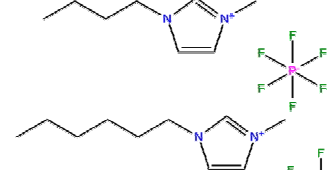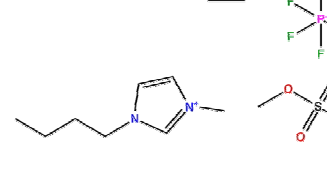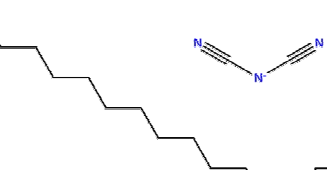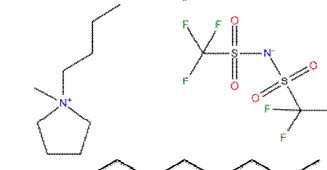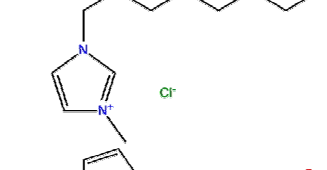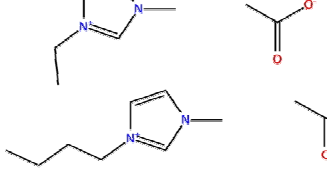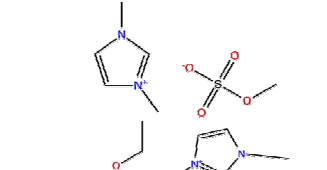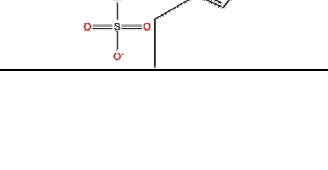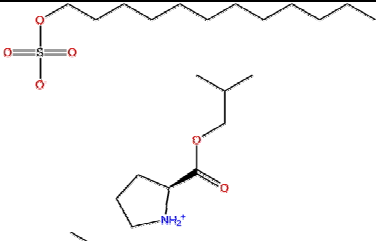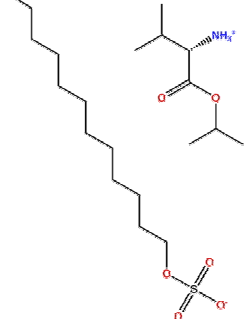
17	1-Octyl-3-methylimidazolium hexafluorophosphate	$C_{12}H_{23}F_6N_2P$	
18	1-Butyl-3-methylimidazolium hexafluorophosphate	$C_8H_{15}F_6N_2P$	
19	1-Hexyl-3-methylimidazolium hexafluorophosphate	$C_{10}H_{19}F_6N_2P$	
20	1-Butyl-3-methylimidazolium methylsulfate	$C_9H_{18}N_2O_4S$	
21	Tetradecyl(trihexyl)phosphonium dicyanamide	$C_{34}H_{68}N_3P$	
22	1-Butyl-1-methylpyrrolidinium bis[(trifluoromethyl)sulfonyl]imide	$C_{11}H_{20}F_6N_2O_4S_2$	
23	1-Methyl-3-octylimidazolium chloride	$C_{12}H_{23}ClN_2$	
24	1-Ethyl-3-methylimidazolium acetate	$C_8H_{14}N_2O_2$	
25	1-Butyl-3-methylimidazolium acetate	$C_{10}H_{18}N_2O_2$	
26	1,3-Dimethylimidazolium methylsulfate	$C_6H_{12}N_2O_4S$	
27	1-Ethyl-3-methylimidazolium ethyl sulfate	$C_8H_{16}N_2O_4S$	

Table 1. Continued

28	(S)-2-(Isobutoxycarbonyl)pyrrolidinium dodecyl sulfate	$C_{21}H_{43}NO_6S$	
29	(S)-1-Isopropoxy-3-methyl-1-oxobutan-2-aminium dodecyl sulfate	$C_{20}H_{43}NO_6S$	

The Group Contribution Method

Development of the thermodynamic models for both pure components and mixtures requires the knowledge of the critical properties and other physical parameters. As stated above, these properties cannot be measured for ionic liquids but are still needed in modeling and correlating experimental data on ionic liquid properties and mixtures containing ionic liquids. The so-called group contribution methods have been commonly used to estimate the critical properties of many substances for the properties which are not available. The method named "modified Lydersen-Joback-Reid" method [24] is proved to give good results for molecules of high molecular weight. The modified Lydersen-Joback-Reid method is summarized in the following three equations:

$$T_b = 198.2 + \sum n \, \Delta T_{bM} \qquad (2)$$

$$T_c = \frac{T_b}{\left[A_M + B_M \sum n \Delta T_M - \left(\sum n \Delta T_m \right)^2 \right]} \qquad (3)$$

$$P_c = \frac{Mw}{\left(C_M + \sum n \Delta P_M \right)^2} \qquad (4)$$

Where $A_M = 0.5703$, $B_M = 1.0121$, and $C_M = 0.2573$.

The extension of the method has been done in a simple way. Three new groups were included: -B, -SO2, -P. The values of these groups and other required groups are summarized in Table 2.

The Proposed Model for Sonic Speed

This work tried to find a rapid simple equation to estimate sonic speed of the ionic liquids based on experimental data with high accuracy by using boiling temperature, reduced temperature and pressure. There are some available experimental data in literatures [8-23] to allow the proposition of a model for sonic speed of the ionic liquids. After multiple regression analysis, a new equation was suggested as follow:

$$\frac{u}{u_0} = T_b^{a_1} \left[a_2 + a_3 \, P \right] \left(a_4 + a_5 T_r + a_6 T_r^2 \right) \qquad (5)$$

where u is the sonic speed in *m/s*, u_0 is the standard sonic speed in 298.15 *K* and 101.33 *kpa*, $T_r = T/T_c$, is the reduced temperature, T_b is the boiling temperature, P is the pressure in *kpa*, and 6 constant parameters obtained by using Marquardt-Levenberg algorithm minimizing sum of the squared differences between values of the observed and

Table 2. Groups Contribution Method Constants

Groups	ΔT_{bm}	ΔT_m	ΔP_m
Without Rings			
-CH3	23.58	0.0275	0.3031
-CH2-	22.88	0.0159	0.2165
>CH-	21.74	0.0002	0.114
>C<	18.18	-0.0206	0.0539
=CH2	24.96	0.017	0.2493
=CH-	18.25	0.0182	0.1866
=C<	24.14	-0.0003	0.0832
=C=	26.15	-0.0029	0.0934
ΞCH		0.0078	0.1429
ΞC-		0.0078	0.1429
-OH (alcohol)	92.88	0.0723	0.1343
-O-	22.42	0.0051	0.13
>C=O	94.97	0.0247	0.2341
-CHO	72.24	0.0294	0.3128
-COOH	169.06	0.0853	0.4537
-COO-	81.1	0.0377	0.4139
HCOO-		0.036	0.4752
=O (others)	-10.5	0.0273	0.2042
-NH2	73.23	0.0364	0.1692
>NH	50.17	0.0119	0.0322
>N-	11.74	-0.0028	0.0304
-N=	74.6	0.0172	0.1541
-CN	125.66	0.0506	0.3697
-NO2	152.54	0.0448	0.4529
-F	-0.03	0.0228	0.2912
-Cl	38.13	0.0188	0.3738
-Br	66.86	0.0124	0.5799
-I	93.84	0.0148	0.9174
With Rings			
-CH2-	27.15	0.0116	0.1982
>CH-	21.78	0.0081	0.1773
=CH-	26.73	0.0114	0.1693
>C<	21.32	-0.018	0.0139
=C<	31.01	0.0051	0.0955
-O-	31.22	0.0138	0.1371
-OH (phenol)	76.34	0.0291	0.0493

Table 2. Continued

>C=O	94.97	0.0343	0.2751
>NH	52.82	0.0244	0.0724
>N-		0.0063	0.0538
-N=	57.55	-0.0011	0.0559
New Groups			
-B	-24.56	0.0352	0.0348
-P	34.86	-0.0084	0.1776
-SO2	147.24	-0.0563	-0.0606

Table 3. Tuned Coefficients of New Proposed Model

Constant parameters	Values	Standard deviation%
a_1	-0.35882	0.005872
a_2	8.3478	0.762243
a_3	0.000015	0.000002
a_4	1.8714	0.019816
a_5	-2.4686	0.028799
a_6	1.7459	0.000059

predicted values of dependent variables. The constant parameters are presented in Table 3.

We carried out calculations for 29 ionic liquids. The criteria for comparisons are AARD%, ARD%, and RMSD calculated as follows:

$$AARD\% = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{u_{r,i,\exp} - u_{r,i,calc}}{u_{r,i,\exp}}\right| \times 100 \quad (6)$$

$$ARD\% = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{u_{r,i,\exp} - u_{r,i,calc}}{u_{r,i,\exp}}\right) \times 100 \quad (7)$$

$$RMSD = \frac{1}{N}\sqrt{\sum_{i=1}^{N}\left(\frac{u_{r,i,\exp} - u_{r,i,calc}}{u_{r,i,\exp}}\right)^2 \times 100} \quad (8)$$

RESULTS AND DISCUSSION

Calculations were carried out for 29 considered ionic liquids in Table 1. Data are divided into two sections. The first section is for training the new equation and the second section is used for validation and estimation the applicability of the obtained equation. The values of boiling

temperature, critical temperature, critical pressure, and standard sonic speed are presented in Table 4 and were taken from literatures [25] or calculated by Group Contribution Method using Table 2. To compare the accuracy of the presented model, calculated sonic speed for training substances versus corresponded values in data bank has been presented in Fig. 1.

Table 4. Properties of Ionic Liquids Calculated by Group Contribution Using the Method Summarized in Table 2

| No.	Formula	T_b (K)	T_c (K)	P_c (bar)	u_0 (m/s)
1	$C_8H_{19}NO_3$	671.7	855.0	26.91	1548.8
2	$C_7H_{17}NO_3$	648.4	834.3	29.97	1611.3
3	$C_7H_{17}NO_3$	648.8	833.0	29.56	1614.5
4	$C_6H_{15}NO_3$	625.9	811.1	32.79	1690.0
5	$C_4H_{11}NO_3$	575.5	758.9	46.91	1815.3
6	$C_5H_{13}NO_3$	603.0	789.3	36.79	1794.8
7	$C_{11}H_{17}F_6N_3O_4S_2$	885.3	1281.1	25.64	1232.0
8	$C_9H_{13}F_6N_3O_4S_2$	759.3	1135.2	30.46	1236.0
9	$C_8H_{15}F_6N_2P$	486.2	630.7	17.28	1421.0
10	$C_{16}H_{32}N_2O_4S$	895.7	1189.8	20.25	1472.9
11	$C_8H_{15}BF_4N_2$	495.2	643.2	20.38	1557.6
12	$C_{10}H_{15}F_6N_3O_4S_2$	862.4	1269.9	27.65	1227.8
13	$C_8H_{11}F_6N_3O_4S_2$	816.7	1249.3	32.65	1238.8
14	$C_8H_{12}BF_4N$	597.3	765.4	20.54	1641.7
15	$C_{14}H_{24}BF_4N$	576.1	720.5	15.09	1511.4
16	$C_{12}H_{19}F_6N_3O_4S_2$	908.2	1292.8	23.89	1226.8
17	$C_{12}H_{23}F_6N_2P$	646.1	810.8	14.05	1407.8
18	$C_8H_{15}F_6N_2P$	554.6	719.4	17.28	1442.8
19	$C_{10}H_{19}F_6N_2P$	600.3	764.9	15.50	1424.2
20	$C_9H_{18}N_2O_4S$	735.6	1081.6	36.10	1658.4
21	$C_{34}H_{68}N_3P$	1230.9	1525.2	7.65	1526.0
22	$C_{11}H_{20}F_6N_2O_4S_2$	759.8	1093.1	24.25	1269.0
23	$C_{12}H_{23}ClN_2$	649.6	869.4	20.32	1715.0
24	$C_8H_{14}N_2O_2$	578.8	807.1	29.19	1737.0
25	$C_{10}H_{18}N_2O_2$	624.6	847.3	24.45	1650.0
26	$C_6H_{12}N_2O_4S$	666.9	1040.0	52.92	1813.0
27	$C_8H_{16}N_2O_4S$	712.7	1067.5	40.46	1679.0
28	$C_{21}H_{43}NO_6S$	1114.9	1363.9	15.16	1429.2
29	$C_{20}H_{43}NO_6S$	1049.7	1285.1	15.25	1400.5
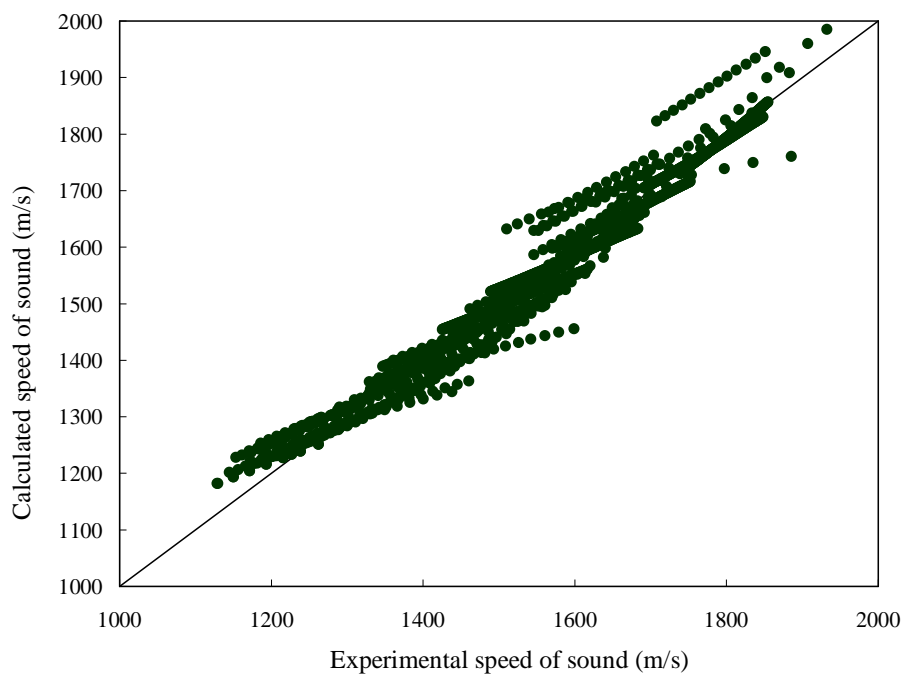
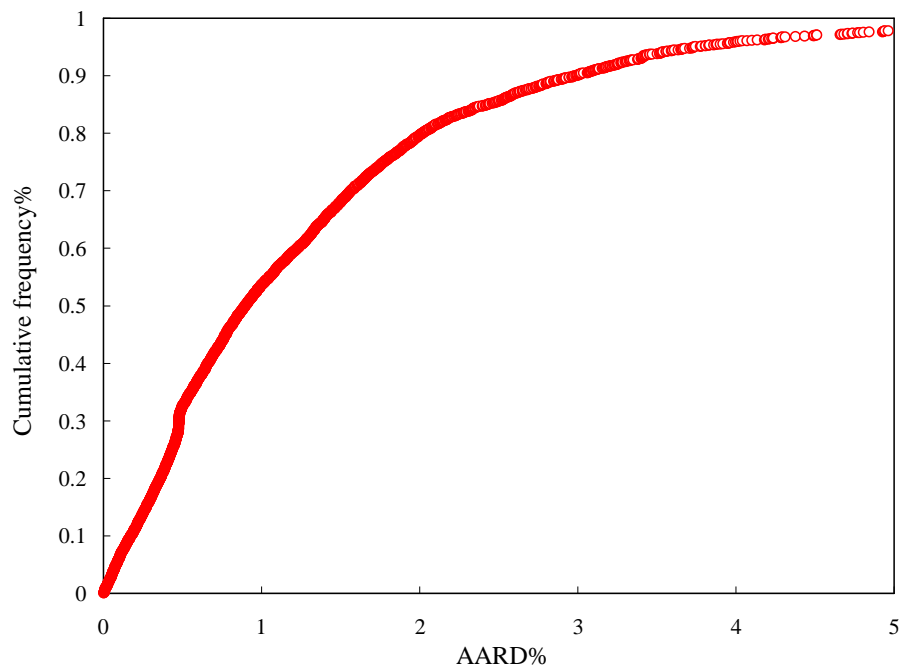**Fig. 1.** Accuracy of presented model *vs.* experimental data.

Fig. 2. AARD% of presented methods in calculating sound speed as a function of cumulative frequency.

Table 5. Properties of Data and AARD% of Validation Set of Ionic Liquids

No.	Formula	Temperature Range (K)	Pressure Range (bar)	Sonic speed range (m/s)	Data point	AARD%	Ref.
1	$C_8H_{15}BF_4N_2$	283.15-343.15	1.00-1513	1462-1882.9	54	1.037	[10]
2	$C_8H_{12}BF_4N$	278.15-338.15	1.0133-1013	1549.5-1691.9	25	0.778	[13]
3	$C_8H_{15}F_6N_2P$	278.15-343.15	1.0133	1329.4-1492.5	27	0.951	[16]
4	$C_{10}H_{19}F_6N_2P$	278.15-343.15	1.0133	1318.4-1490.7	14	1.170	[16]

As shown in Fig. 1, if a solid circle stands on the line, the deviation of this point will be zero. Also the deviation of each data point is increased by the increase of distance from the line. Therefore, Fig. 1 shows that the most of data points are close to the line and have low deviation from experimental values.

In Table 4, temperature range, pressure range, sonic speed range, number of data points, and AARD% of sonic speeds calculated from the proposed model for training data with respect to the values given by experimental data are presented.

Figure 2 shows the cumulative frequency of the proposed corresponding method versus average absolute relative deviations.

Cumulative frequency analysis is performed to obtain insight into how often a certain phenomenon (feature) is placed below a certain value. This may help in describing or explaining 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 to the top left corner of plot square has more accuracy than those in the lower curves.

Figure 2 also shows the accuracy of the proposed method in estimating the sonic speed of 29 pure ionic liquids.

The new method has successfully predicted 79.7% of all 2198 data with AARD% less than 2, and 95.9% of the data with AARD% less than 4. Only 2.1% of the sonic speed data was predicted with AARD% of more than 5 by the new method.

To estimate the applicability of the new correlation for calculating sonic speed of various ionic liquids, the experimental data of four ionic liquids, not employed in regression analysis of new proposed empirical correlation, are used for calculating sonic speed to validate the new presented equation.

Temperature range, pressure range, sonic speed range, number of data points, and the AARD% of sonic speeds calculated from the proposed model for validation data with respect to the values given by experimental data are presented in Table 5.

CONCLUSIONS

In this study, a database for the sonic speed of pure ionic liquids was considered. By using this database, a new equation was developed to predict the sonic speed for several pure ionic liquids. The presented equation is a 6-variable linear model which has been developed based on the 2198 experimental data for 29 pure ionic liquids as a function of boiling temperature, reduced temperature and pressure. To consider the new method, the speeds of sound of the considered ionic liquids were examined and an overall average absolute relative deviation of 1.30%, a coefficient of determination (R^2) of 0.987, and a root mean square error (RSMD) of 1.85 was achieved. For estimating the applicability of the new correlation, the experimental data of four ionic liquids, not employed in regression analysis, were used for calculating sonic speed to validate the new presented equation.

ACKNOWLEDGEMENTS

acknowledged.

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