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A group contribution-based prediction method for the electrical conductivity of ionic liquids

Yuqiu Chen, Yingjun Cai, Kaj Thomsen, Georgios M. Kontogeorgis, John M. Woodley*

Department of Chemical and Biochemical Engineering, Technical University of Denmark

DK-2800 Lyngby, Denmark

*Corresponding author. Tel.: +45 45252885. E-mail address: jw@kt.dtu.dk (J.M. Woodley)

Abstract

A group contribution method is developed for estimating the electrical conductivity of ionic liquids (ILs). Based on 1578 collected experimental data covering 57 ILs in a wide range of temperature (248.05–468.15K) and electrical conductivity ($0.0017\text{--}9.1670\text{ S}\cdot\text{m}^{-1}$), the parameters of each group (cation, anion, substituent) in the method are optimized. A deterministic algorithm-based on multivariate linear regression is used with 1121 data points covering 57 ILs used as training set and the remaining 457 data points covering 20 ILs are used for validation. The prediction results (from test set) expressed as an average absolute relative deviation (AARD %) of 6.8% between the experimental and predicted electrical conductivities of ILs illustrate the good predictive capability of this group contribution method, with a maximum relative deviation (RD %) of 26.6%. This group contribution-based method can be easily extended to new IL groups that are not involved in this study once the experimental data of ILs involving these new groups become available.

Keywords: Ionic liquids; group contribution method; electrical conductivity; property prediction

1. Introduction

Ionic liquids (ILs) with various unique properties (e.g. negligible vapor pressure, high stability and wide electrochemical window) [1] are being considered as potential alternatives to conventional organic solvents in many fields such as chemical [2, 3], biochemical [4–7], pharmaceutical [8] and electrochemical industry [9–12]. As “designer solvents”, ILs offer numerous opportunities for the existing process modification and for the new process development since specific-task IL solvents with desired physical and thermo-physical properties are possibly designed by tuning their group combinations. As applications of ILs are increasing rapidly in many scientific fields, it is important to understand their behaviour in the systems involving these compounds. Therefore, study of property characterization and structure-property relationships for ILs is as important as the investigation of their applications. Meanwhile, the development of predictive property methods makes it possible to use the computer-aided IL design (CAILD) method [13], which can efficiently screen or design suitable ILs with a set of desired properties for specific tasks.

Due to the unique features, ILs open the possibility of improving ion conductive materials which are basically needed in electro chemistry [14]. Electrical conductivity is the measure of a material's ability to allow the transport of an electric charge and it is a critical property in electronic applications. With a rising interest of ILs in electro chemistry, a systematic knowledge of their electrical conductivities is of great importance. ILs. In addition, experimentally measured electrical conductivity of ILs are not available for However, only a limited number of ILs have been synthesized, and information on their electrical conductivities is restricted to only some well-known all potential IL candidates. On the other hand, the modeling of electrical conductivity is a cost-effective method for determining electrical conductivity in IL materials. While a variety of methods (e.g. simulation methods, analytical–mathematical methods, and image processing methods) have been developed for modeling of electrical conductivity in composites [15], the modeling work of electrical conductivity for IL materials is of importance as well but has lagged behind.

Several methods have been successfully proposed for property prediction (e.g. viscosity, heat capacity) [16-18] of ILs. Group contribution-based methods are popular because they are simple methods, easy to use, have some predictive capabilities [19]. For the electrical conductivity of ILs, Gardas and Coutinho employed a Vogel-Tammann-Fulcher (VTF) type equation with a good overall result [20]. However, only 4 cations, 7 anions and 1 side group were studied and the predictive performance of this method was not fully established. Considering the importance of the modeling of the electrical conductivity of ILs, it is the purpose of this work to develop a reliable and predictive group contribution method for the estimation of this property., which can be used for a wider range of ILs, both well-known ILs and others never studied before.

In the present work, we extend our database [18] with some new ILs and a wide range of experimental data containing electrical conductivity. To evaluate the predictive performance of the proposed group contribution-based method, all ILs containing experimental data of electrical conductivity in the database were extracted, wherein nearly 70% of the datasets are used for the purpose of generating optimum group parameters and the remaining datasets are used for validating the predictive performance of this method.

All IL ions and substituents involved in the studying of electrical conductivity are summarized as following; cations: imidazolium [Im], pyridinium [Py], pyrrolidinium [Pyr], alkyl ammonium [N], alkyl phosphonium [P], sulfonium [S]; piperidinium [Pip] and morpholin [Morp]; anions: bis(trifluoromethanesulfonyl) amide [Tf₂N], tetrafluoroborate [BF₄], hexafluorophosphate [PF₆], chloride [Cl], bromide [Br], iodide [I], formate [COO], acetate [C₁COO], propanoate [C₂COO], butanoate [C₃COO], hexanoate [C₅COO], octanoate [C₇COO], decanoate [C₉COO], methyl sulfate [MeSO₄], ethyl sulfate [EtSO₄], octyl sulfate [C₈SO₄], trifluoromethanesulfonate [CF₃SO₃], trifluoroacetate [CF₃COO], methanesulfonate [CH₃SO₃], dicyanamide [N(CN)₂], tricyanomethanide [C(CN)₃], tetracyanoborate [B(CN)₄], ethyl phosphonate [C₂PO₃], butyl phosphonate [C₄PO₃], hexylphosphonate [C₆PO₃], octyl phosphonate [C₈PO₃], bis(perfluoroethylsulfonyl)imide [Pf₂N], dihydrogen phosphate [(OH)₂PO₂], tris(pentafluoroethyl)trifluorophosphate [eFAP], hydrogen carbonate [OHCO₂], nitrate [NO₃], bis(fluorosulfonyl)amide [TS₂N], tosylate [Tos], and thiocyanate [SCN]; substituents: methyl (-CH₃), methylene (-CH₂-), hydroxy (-OH), methoxymethyl (-CH₂OCH₃). Figure 1 presents the chemical structures of the cation cores belonging to the ILs studied in this work.

Figure 1. Chemical structures of the cation cores belonging to the studied ILs

2. Results and discussion

In this work, a group contribution-based model (Eq. 1), similar to the equation previously used with success for the viscosity [18], is used for the prediction of electrical conductivity of ILs considering the connection between these two properties [20].

$$\ln \frac{\varepsilon}{R_{0\varepsilon}} = A_\varepsilon + B_\varepsilon \frac{100}{T} + C_\varepsilon \left(\frac{100}{T} \right)^2 \quad 1$$

where ε is the electrical conductivity in $\text{S}\cdot\text{m}^{-1}$ and T is the temperature in K. $R_{0\varepsilon}$ is an adjustable parameter, also with a unit of $\text{S}\cdot\text{m}^{-1}$. A_ε , B_ε and C_ε are calculated from the group contribution method, as shown in Eq.2.

$$A_\varepsilon = \sum_{i=1}^k n_i a_{i,\varepsilon} \quad B_\varepsilon = \sum_{i=1}^k n_i b_{i,\varepsilon} \quad C_\varepsilon = \sum_{i=1}^k n_i c_{i,\varepsilon} \quad 2$$

where k is the number of all groups contained in the molecule and n_i is the number of groups of type i . The group contributions $a_{i,\varepsilon}$, $b_{i,\varepsilon}$ and $c_{i,\varepsilon}$ are obtained by correlating the experimental data points into Eq.1 using average absolute relative deviation (AARD%) Eq.3 is used as the objective function.

$$O.F. = \frac{100\%}{N} \sum_{i=1}^N \left| \left(\exp \left(A_\varepsilon + B_\varepsilon \frac{100}{T} + C_\varepsilon \left(\frac{100}{T} \right)^2 \right) * R_{0\varepsilon} - \varepsilon_{exp} \right) / \varepsilon_{exp} \right|_i \quad 3$$

where N represents the number of the experimental data points for correlation.

The 1578 experimental data points of electrical conductivity from the database, as presented in Table 1, include 77 ILs covering 8 cation cores, 34 anions and 4 side groups in a wide range of temperature, 248.05-468.15 K and electrical conductivity, 0.0017-9.167 $\text{S}\cdot\text{m}^{-1}$. The detailed information of these data are provided in Supplementary material. Among these data points, a training set consisting of 1121 data points for 57 ILs is used to correlate the group contribution model (Eq.1). The resulting AARD (%) of this correlation is 3.30% with a maximum relative deviation (RD) % of -27.6% which shows the availability of the generated group contribution parameters. The parameters are presented in Table 2.

Table 1. Correlation of electrical conductivity for all 77 ionic liquids using Eq.1 and their calculated electrical conductivity at 298.15 K

Ionic Liquid	Temperature Range (K)	Data Points	Relative Deviation (%)	Average Absolute Relative Deviation (%)	Calculated Electrical Conductivity at 298.15 K ($\text{S}\cdot\text{m}^{-1}$)	Reference
[C2mIm][Tf2N]	293.15-353.15	4	-8.4; 18.2	9.23	0.744	[21]
[C4mIm][Tf2N]	283.15-348.15	7	-26.6; 1.5	8.14	0.397	[22]
	298.15-353.15	56	-1.6; 1.6	1.02		[23]
	273.15-353.17	51	-19.8; 1.7	5.31		[22]
	263.0-373.0	10	-22.7; -4.4	10.66		[24]
	293.15-328.15	8	-13.8; 4.0	6.58		[25]
	293.15-323.15	7	-11.6; 4.0	5.54		[26]
	297.95-372.43	5	1.3; 2.9	2.04		[27]
	288.15-323.15	5	-0.8; 2.3	1.72		[28]
	283.15-333.15	4	-4.0; 1.7	1.55		[29]
	278.15-408.15	14	-4.4; 4.0	2.09		[30]
[C6mIm][Tf2N]	263.0-373.0	10	-20.2; 3.8	4.85	0.212	[24]
	278.15-323.15	9	-5.2; 3.7	2.78		[31]
	293.15-323.15	7	3.3; 5.2	4.50		[32]

	288.15-323.15	5	0.0; 4.2	2.54		[33]
	288.15-323.15	5	0.0; 3.8	2.40		[28]
[C ₈ mIm][Tf ₂ N]	263.0-373.0	10	-10.3; 14.7	11.50	0.113	[30]
[OHC ₁ mIm][Tf ₂ N]	283.15-353.15	15	-2.6; 2.1	0.82	0.092	[34]
[C ₄ mIm][BF ₄]	303.15-353.15	11	-10.5; 15.8	6.80	0.223	[35]
[C ₆ mIm][BF ₄]	248.05-468.15	23	-27.7; 6.4	4.11		[36]
	303.0-333.0	7	0.9; 3.4	2.06	0.119	[37]
	298.15	1	5.6	5.60		[38]
	298.15	1	3.1	3.10		[39]
[C ₈ mIm][BF ₄]	298.15-348.15	24	-20.3; 9.0	7.65		[40]
	268.10-468.15	7	-2.6; -1.7	2.09	0.063	[37]
	298.15	1	8.1	8.10		[41]
[C ₁₀ mIm][BF ₄]	263.10-353.10	33	-0.6; 8.1	3.10	0.034	[42]
[C ₂ mIm][PF ₆]	356.50-423.10	16	-10.2; 25.0	9.00	0.171	[42]
[C ₄ mIm][PF ₆]	328.15-468.15	15	-1.9; 23.4	5.95	0.091	[43]
[C ₆ mIm][PF ₆]	273.00-353.18	48	-15.1; 14.2	6.32		[44]
	293.15-343.15	11	0.1; 11.3	6.45	0.049	[45]
	303.0-333.0	7	2.5; 11.3	6.91		[37]
[C ₈ mIm][PF ₆]	273.20-353.17	57	-12.5; 1.6	2.60	0.026	[40]
[C ₂ mIm][Cl]	333.50-433.10	21	-1.4; 3.9	0.68	0.108	[42]
[C ₂ mIm][Br]	258.10-330.90	28	-21.7; 17.2	8.67	0.031	[42]
[C ₂ mIm][I]	258.60-308.10	17	-22.1; 5.8	4.48	0.010	[42]
[C ₂ mIm][eFAP]	278.15-458.15	19	-10.9; 4.2	1.84	0.548	[30]
[C ₆ mIm][eFAP]	293.15-343.15	11	2.7; 18.5	13.37	0.156	[45]
[C ₄ mIm][CF ₃ COO]	298.15-348.15	11	-1.0; 1.1	0.41	0.454	[46]
[C ₄ mIm][CF ₃ SO ₃]	283.15-333.15	21	-7.9; 6.0	2.61		[43]
	268.15-468.15	10	-6.8; 1.2	2.54	0.288	[24]
[C ₄ mIm][N(CN) ₂]	273.15-323.15	7	0.0; 2.5	1.37	1.145	[47]
[C ₂ mIm][C(CN) ₃]	298.0-333.0	5	-0.09; 4.3	1.37	0.765	[48]
[C ₂ mIm][B(CN) ₄]	273.15-353.15	12	-6.4; 1.2	1.27	1.538	[49]
[C ₃ mIm][OHCO ₂]	288.15-343.15	12	-10.3; 19.9	8.59	0.523	[50]
[C ₄ mIm][OHCO ₂]	288.15-343.15	12	-2.6; 0.3	0.62	0.382	[50]
[C ₅ mIm][OHCO ₂]	298.15-343.15	10	-12.4; 7.5	6.12	0.279	[50]
[C ₃ mIm][(OH) ₂ PO ₂]	288.15-343.15	12	0.0; 8.0	3.41	0.578	[50]
[C ₄ mIm][(OH) ₂ PO ₂]	288.15-343.15	12	-2.6; 0.0	1.00	0.422	[50]
[mmIm][MeSO ₄]	278.15-368.15	10	-3.3; 6.5	2.89	0.376	[51]
[C ₄ mIm][MeSO ₄]	293.15-343.15	6	-11.3; 21.1	10.30		[52]
	298.15-343.15	6	-16.2; 7.9	8.48	0.146	[53]
	298.15	1	-16.2	16.20		[54]
[C ₂ mIm][EtSO ₄]	258.10-433.10	36	-26.1; 7.1	4.83		[55]
	293.20-353.20	11	-5.3; 7.9	3.97		[56]
	298.15-323.15	6	-2.6; 3.8	2.02	0.366	[57]
	298.15	1	8.1	8.10		[58]
[C ₂ mIm][C ₈ SO ₄]	258.10-373.10	24	-8.1; 3.4	1.35	0.045	[59]
[C ₂ mIm][CH ₃ SO ₃]	273.15-353.15	19	-5.3; 2.5	1.33	0.259	[60]
[C ₄ mIm][C ₁ COO]	283.15-323.15	9	-2.3; 1.7	0.76		[61]
	278.15-358.15	9	-16.5; 7.3	8.81	0.049	[62]
[C ₄ mIm][COO]	308.15-343.15	8	-15.6; 5.7	6.03	0.185	[63]
[C ₄ mIm][C ₂ COO]	303.15-343.15	9	-3.1; 1.1	0.75	0.052	[63]
[C ₄ mIm][C ₃ COO]	303.15-343.15	9	-1.8; 0.7	0.43	0.029	[63]
[C ₂ mIm][Tos]	278.15-368.15	10	-2.4; 3.1	1.19	0.085	[51]
[C ₃ mmIm][SCN]	288.15-323.15	8	-5.1; 2.0	0.99	0.458	[64]
[C ₂ Py][Tf ₂ N]	293.15-338.15	10	-12.7; 6.8	6.80		[65]
	298.15	2	8.4; 8.6	8.50	0.576	[66]
[C ₃ Py][Tf ₂ N]	313.15-338.15	6	-12.0; -3.1	7.67	0.420	[67]
[C ₄ Py][Tf ₂ N]	278.15-438.15	15	-0.8; 9.1	2.95		[68]
	283.15-338.15	12	-1.4; 10.2	2.82		[65]
	263.0-373.0	10	-3.9; 7.0	4.52	0.307	[24]
	283.15-313.15	15	-2.0; 0.7	0.78		[66]

[C ₅ Py][Tf ₂ N]	283.15-338.15	12	-7.3; -0.7	2.28		[65]
	298.15	1	-3.8	3.80	0.224	[66]
[C ₆ Py][Tf ₂ N]	283.15-338.15	12	-0.9; 6.2	3.06		[67]
	283.15-313.15	6	-4.0; 0.6	1.15	0.164	[66]
[C ₂ Py][CF ₃ SO ₃]	293.15-338.15	19	7.7; 18.5	12.88	0.418	[69]
[C ₄ Py][CF ₃ SO ₃]	303.15-338.15	15	-5.1; 2.4	1.99	0.222	[70]
[C ₄ mPy][Tf ₂ N]	278.15-363.15	16	-11.4; 24.2	9.58	0.239	[71]
[C ₈ mPy][BF ₄]	278.15-338.15	25	-10.5; 3.9	2.27	0.038	[70]
[C ₃ mPy][Tf ₂ N]	278.15-353.15	11	-2.2; 8.9	4.48		[72]
	293.15-353.15	4	-3.4; 4.7	2.65	0.378	[21]
[C ₄ mPy][Tf ₂ N]	298.15-353.15	56	-1.3; 6.2	1.28		[23]
	273.15-353.15	13	-2.3; 0.2	0.83		[73]
	293.15-453.15	11	-15.7; 13.2	9.68		[74]
	263.0-373.0	10	-3.9; 2.4	1.56	0.276	[24]
	293.40-333.50	9	-2.7; -1.5	2.16		[75]
	298.15-323.15	6	-0.8; 0.3	0.33		[76]
	293.15-353.15	4	-13.8; 0.4	6.65		[21]
[C ₆ mPy][Tf ₂ N]	293.15-353.15	4	0.2; 3.8	1.95	0.147	[21]
[C ₈ mPy][Tf ₂ N]	295.10	1	3.4	3.40	0.078	[77]
[COCC ₄ mPy][Tf ₂ N]	298.15-353.15	7	-2.0; 15.6	6.57	0.292	[78]
[C ₂ mPy][C ₂ PO ₃]	293.18-323.13	13	-1.2; 9.0	2.42	0.227	[79]
[C ₄ mPy][C ₄ PO ₃]	293.18-323.13	13	-3.0; 3.6	1.87	0.027	[79]
[C ₆ mPy][C ₆ PO ₃]	293.18-323.13	13	-1.6; 0.6	0.40	0.037	[79]
[C ₈ mPy][C ₈ PO ₃]	293.18-323.13	13	-1.1; 2.8	0.68	0.034	[79]
[C ₄ mPy][TS ₂ N]	298.15-361.15	10	-0.1; 11.9	4.39	0.763	[80]
[COC ₄ mPy][TS ₂ N]	273.15-333.15	10	-7.2; 18.6	6.17	1.104	[81]
[Am(2)][NO ₃]	312.83-325.72	44	-0.03; 0.3	0.04	2.328	[82]
[Am(5)112][Tf ₂ N]	273.15-353.15	12	-5.1; -0.03	2.38	1.142	[83]
[Am(3)][COO]	293.15-333.15	9	-2.1; 3.4	1.12	0.360	[84]
[2.2.2.5Ph][Tf ₂ N]	283.15-348.16	42	-1.6; 1.3	0.41		[85]
	298.15-361.15	10	0.4; 21.4	12.42	0.165	[80]
[2.2.2.5Ph][TS ₂ N]	298.15-361.15	10	-7.3; 1.5	4.49	0.456	[80]
[TDPH][C ₅ COO]	299.60-349.30	11	-4.1; 2.0	1.23	0.003	[86]
[TDPH][C ₇ COO]	300.60-349.50	11	-10.4; 5.8	2.32	0.002	[86]
[TDPH][C ₉ COO]	298.80-349.70	11	-5.4; 2.9	1.56	0.002	[86]
[S222][Tf ₂ N]	258.15-468.15	22	-15.3; 4.3	2.63	0.684	[68]
[C ₄ mPip][C ₄ PO ₃]	293.15-323.15	13	-2.8; 3.9	1.49	0.031	[79]
[C ₂ mmorp][C ₂ PO ₃]	293.15-323.15	13	-1.7; 3.8	1.23	0.095	[79]
[C ₈ mmorp][C ₈ PO ₃]	293.15-323.15	13	-1.8; 2.1	0.83	0.018	[79]
[C ₄ mIm][Pf ₂ N]	273.15-338.15	29	-7.6; 4.8	2.08	0.142	[30]
[C ₂ Py][N(CN) ₂]	298.15-338.15	9	-4.5; 3.3	3.39	1.661	[87]
[C ₃ Py][N(CN) ₂]	298.15-338.15	9	2.0; 7.3	4.49	1.213	[87]
[C ₄ Py][N(CN) ₂]	298.15-338.15	9	-4.8; 1.3	2.34	0.886	[87]
[C ₆ Py][N(CN) ₂]	298.15-338.15	9	-2.7; 2.4	1.47	0.472	[87]
[Am(7)112][Tf ₂ N]	273.25-353.25	12	4.8; 9.9	7.05	0.076	[83]
Total	248.05-468.15	1578	-27.7; 25.0	3.62		

Table 2: Group contributions with a $R_{0\epsilon}$ of 14.065 generated from training set and used for the prediction of test set

Groups	$a_{i,\epsilon}$	$b_{i,\epsilon}$ (K)	$c_{i,\epsilon}$ (K ²)
Cation cores			
Im (+)	-2.758	-2.382	-20.946
Py (+)	-8.161	32.294	-84.506
Pyr (+)	-9.70	21.129	-50.539
N (+)	-5.805	17.862	-49.300
P (+)	-1.526	-9.956	2.154

S (+)	0.558	-20.044	16.88
Pip (+)	-8.551	0.946	-6.66
Morp (+)	-4.899	-11.179	-3.838
Substituents			
(ring)-H	0.542	0.284	-1.976
-CH ₃	-1.113	13.728	-29.784
-CH ₂ -	-0.370	1.575	-4.231
-OH	-15.245	112.970	-218.674
-CH ₂ OCH ₃	-4.986	26.105	-38.415
Anions			
[Tf ₂ N] ⁻	2.455	-5.018	8.866
[BF ₄] ⁻	0.976	12.771	-35.893
[PF ₆] ⁻	0.264	19.192	-56.048
[Cl] ⁻	-13.292	120.824	-246.724
[Br] ⁻	4.775	-32.691	42.637
[I] ⁻	-4.089	0.017	13.391
[COO] ⁻	4.626	-16.219	15.635
[C ₁ COO] ⁻	-18.432	138.818	-252.907
[C ₂ COO] ⁻	2.625	1.624	-30.474
[C ₃ COO] ⁻	2.302	6.065	-45.897
[C ₅ COO] ⁻	6.720	-26.121	58.591
[C ₇ COO] ⁻	5.996	-21.580	48.535
[C ₉ COO] ⁻	8.487	-41.999	84.764
[MeSO ₄] ⁻	1.299	5.502	-22.042
[EtSO ₄] ⁻	-1.167	21.910	-45.589
[C ₈ SO ₄] ⁻	-2.187	25.535	-65.878
[CF ₃ SO ₃] ⁻	1.926	-0.101	-3.858
[CF ₃ COO] ⁻	1.472	1.768	-1.387
[CH ₃ SO ₃] ⁻	-9.062	75.654	-138.689
[N(CN) ₂] ⁻	0.159	12.183	-12.422
[C(CN) ₃] ⁻	1.396	1.849	-2.001
[B(CN) ₄] ⁻	-0.171	10.987	-9.115
[C ₂ PO ₃] ⁻	0.712	-4.657	15.829
[C ₄ PO ₃] ⁻	1.193	-5.456	0.238
[C ₆ PO ₃] ⁻	18.032	-128.276	225.298
[C ₈ PO ₃] ⁻	1.044	-23.294	68.207
[Pf ₂ N] ⁻	1.134	4.069	-15.611
[eFAP] ⁻	2.362	-7.543	14.190
[OHCO ₂] ⁻	-2.995	13.091	4.157
[(OH) ₂ PO ₂] ⁻	3.337	-20.140	47.179
[NO ₃] ⁻	2.980	-1.589	0.402
[TS ₂ N] ⁻	-0.715	16.175	-17.120
[Tos] ⁻	-10.417	82.771	-157.692
[SCN] ⁻	2.494	0.995	-8.514

To evaluate the predictive performance of this model for the electrical conductivity, the obtained group contribution parameters from the training set are used to predict the electrical conductivity of another 20 ILs (457 data points) used as test set. The resulting AARD (%) of the prediction is 6.8% with a maximum RD (%) of 26.6%, showing that the experimental electrical conductivity can be described well by this group contribution-based method. For both the training and test sets, comparison between experimental and calculated electrical conductivities of ILs and their

corresponding distributions of relative deviations between experimental data and model calculations are presented are shown in Figure 2.

Figure 2. Plots of experimental versus calculated electrical conductivities for ILs and relative deviations between experimental and calculated data from Eq.1 using parameters given in Table 2: (a) training set; (b) relative deviations for training set; (c) test set; (d) and relative deviations for test set.

After having proved the predictive capability of the method and in order to improve the reliability of the parameters of each group involved, all 1578 data points containing 77 ILs are applied as correlation dataset. In this correlation which covers the total dataset, the generated group contribution parameters $a_{i,\varepsilon}$, $b_{i,\varepsilon}$ and $d_{i,\varepsilon}$ with the $R_{0\varepsilon}$ of $7.175 \text{ S} \cdot \text{m}^{-1}$ are given in Table 3.

The AARD (%) of this correlation is 3.6% and the maximum RD (%) is 27.7% observed for 1-hexyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_6\text{mIm}][\text{BF}_4]$) at 248.05 K. As presented in Figure 3, among all 1578 data points, 61.8% of the calculated electrical conductivities are within relative deviation of 0.00–3.0%, 24.2% within 3.0–8.0%, 13.0% within 8.0–20.0%, and only 0.9% of the calculated electrical conductivities have larger than 20.0% deviation. As mentioned by Gardas and Coutinho [20], some of the observed larger deviations may come from the presence of water since its appearance in IL sample can significantly improve the electrical conductivity[88].

Figure 3. (a) Comparison between experimental and calculated electrical conductivities with parameters given in Table 3 for all 1578 data points and (b) relative deviations between the experimental and calculated electrical conductivities as a function of experimental electrical conductivities.

Table 3: Proposed group contributions with a $R_{0\epsilon}$ of 7.175 from all datasets in parameter regression

Groups	$a_{i,\epsilon}$	$b_{i,\epsilon}$ (K)	$c_{i,\epsilon}$ (K ²)
Cation cores			
Im (+)	-3.395	-2.203	-20.040
Py (+)	-8.186	27.411	-75.921
Pyr (+)	-11.433	22.238	-53.087
N (+)	-6.350	18.130	-47.838
P (+)	-2.374	-8.287	2.510
S (+)	0.217	-20.101	19.628
Pip (+)	-10.215	0.634	-9.746
Morp (+)	-7.063	-8.805	-3.713
Substituents			
(ring)-H	0.768	0.239	-1.863
-CH ₃	-0.916	14.681	-32.162
-CH ₂ -	-0.261	0.818	-2.914
-OH	-15.037	113.352	-219.442
-CH ₂ OCH ₃	-14.857	87.076	-129.174
Anions			
[Tf ₂ N] ⁻	2.434	-4.774	8.068
[BF ₄] ⁻	1.004	12.416	-35.592
[PF ₆] ⁻	-0.712	26.779	-71.130
[Cl] ⁻	-5.238	61.590	-138.793
[Br] ⁻	9.181	-58.797	81.002
[I] ⁻	-4.199	0.039	14.055
[COO] ⁻	4.746	-16.881	16.851
[C ₁ COO] ⁻	-18.287	137.632	-250.943
[C ₂ COO] ⁻	2.586	1.629	-30.423
[C ₃ COO] ⁻	2.232	6.316	-46.319
[C ₅ COO] ⁻	7.528	-30.348	62.526
[C ₇ COO] ⁻	6.315	-24.051	52.043
[C ₉ COO] ⁻	8.680	-42.717	83.824
[MeSO ₄] ⁻	0.663	5.064	-14.378

[EtSO ₄] ⁻	-0.901	19.849	-42.019
[C ₈ SO ₄] ⁻	-2.117	24.723	-64.297
[CF ₃ SO ₃] ⁻	1.935	-0.173	-4.067
[CF ₃ COO] ⁻	1.445	1.756	-1.403
[CH ₃ SO ₃] ⁻	-9.465	77.852	-141.887
[N(CN) ₂] ⁻	0.384	10.832	-10.825
[C(CN) ₃] ⁻	1.209	2.114	-1.333
[B(CN) ₄] ⁻	-0.526	12.808	-11.593
[C ₂ PO ₃] ⁻	1.020	-5.226	14.679
[C ₄ PO ₃] ⁻	0.433	-3.128	0.337
[C ₆ PO ₃] ⁻	19.378	-137.830	241.937
[C ₈ PO ₃] ⁻	1.111	-23.714	68.857
[Pf ₂ N] ⁻	1.179	3.507	-14.629
[eFAP] ⁻	2.392	-8.346	16.376
[OHCO ₂] ⁻	-1.491	8.359	3.457
[(OH) ₂ PO ₂] ⁻	3.303	-19.117	43.664
[NO ₃] ⁻	3.193	-2.012	0.138
[TS ₂ N] ⁻	-0.920	16.681	-17.053
[Tos] ⁻	-10.515	83.229	-158.476
[SCN] ⁻	2.298	1.030	-7.327

As shown in Figure 3, the electrical conductivity of ILs increases with the increase of temperature and this increase is more significant at higher temperatures since high temperature liquids generally have high fluidity and therefore high conductivity would be expected according to the Walden rule [89]. In addition, the electrical conductivity of ILs decreases with the increase of the side chain length on the cation or anion, which can be explained as the viscosity of ILs increases with the increase of the side chain length [18].

Figure 3. Comparisons of experimental data [35, 37, 42, 61, 63] and calculated values for $\epsilon - T$ covering (a) $[C_n\text{mlm}][\text{BF}_4]$ ($n=4, 6, 8, 10$), (b) $[C_4\text{mlm}][C_n\text{COO}]$ ($n=0, 1, 2, 3$). Lines are calculation results using the predictive method developed in this work with parameters shown in Table 3.

To compare the performance of the proposed method with the method developed by Gardas and Coutinho [20], we compiled the number of fitted and predicted data points and the AARD%, shown as in Table 4. The comparisons reflect the improvements and the reliability of the group contribution method for electrical conductivity proposed in this work.

Table 4. Comparison between the methods used in this work and the work of Gardas and Coutinho [20]

Properties	Author(s)	Sets	Calculation types	Data Points	ILs	AARD (%)
Electrical conductivity	Gardas and Coutinho	Total	Correlation	307	15	4.57
		Training	Correlation	Not provided		
		Test	Prediction	Not provided		
	This work	Total	Correlation (Table 3)	1578	77	3.62
		Training	Correlation (Table 2)	1121	57	3.30
		Test	Prediction (Table 2)	457	20	6.83

3. Conclusion

This work presents a group contribution-based prediction method for the electrical conductivity of ILs. More than 1500 experimental data points from 77 ILs covering 8 cations, 34 anions and 4 substituents in a wide range of temperature (293.15–393.15K) were employed for verifying this method. The resulting AARD (%) of prediction is 6.8%, showing that the experimental electrical conductivity can be described well by the proposed method. This method can predict the electrical conductivities of ILs, both well-known ILs and for those not previously studied. This makes it possible to use CAILD method for the design of suitable ILs rapidly and confidently for their applications in electrochemical industry. In addition, the generated optimum parameters in the method provide a direct perception of each group for their contributions to the electrical conductivity. Still, this method can be further extended to new groups (i.e. cation, anion, substituent) of ILs, once more experimental data become available.

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Supplementary material

Tables summarizing the information of the collected experimental data containing electrical conductivity of ionic liquids. These data are used to regress the contribution parameters of each involved group in the proposed model.

Appendix A: Calculation Examples

Example 1. 1-(2-methoxyethyl)-1-methylpyrrolidinium bis((trifluoromethyl)sulfonyl)amide at 323.15 K

Group Assignment	$R_{0\varepsilon} = 7.175$			
	n_i	$a_{i,\varepsilon}$	$b_{i,\varepsilon}$ (K)	$c_{i,\varepsilon}$ (K ²)
Cations				
Pyr (+)	1	-11.433	22.238	-53.087
Substituents				
(ring)-H	8	0.768	0.239	-1.863
-CH ₃	1	-0.916	14.681	-32.162
-CH ₂ -	1	-0.261	0.818	-2.914
-CH ₂ OCH ₃	1	-14.857	87.076	-129.174
Anions				
[Tf ₂ N] ⁻	1	2.434	-4.774	8.068

$$A_{\varepsilon} = \sum_{i=1}^k n_i a_{i,\varepsilon} = (-11.433) + (0.768 \times 8) + (-0.916) + (-0.261) + (-14.857) + 2.434 = -18.889$$

$$B_{\varepsilon} = \sum_{i=1}^k n_i b_{i,\varepsilon} = 22.238 + (0.239 \times 8) + 14.681 + 0.818 + 87.076 + (-4.774) = 121.951$$

$$C_{\varepsilon} = \sum_{i=1}^k n_i c_{i,\varepsilon} = (-53.087) + (-1.863 \times 8) + (-32.162) + (-2.914) + (-129.174) + 8.068 \\ = -224.173$$

$$\varepsilon = \exp \left(A_{\varepsilon} + B_{\varepsilon} \frac{100}{T} + C_{\varepsilon} \left(\frac{100}{T} \right)^2 \right) * R_{0\varepsilon} = \left((-18.889) + 121.951 \times \frac{100}{323.15} + (-224.173) \times \left(\frac{100}{323.15} \right)^2 \right) \times \\ 7.175 = 0.523 \text{ S} \cdot \text{m}^{-1}$$

Experimental value [30]: $0.534 \text{ S} \cdot \text{m}^{-1}$

RD(%): 1.98%

Example 2. 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate at 298.15 K

Group Assignment	$R_{0\varepsilon} = 7.175$			
	n_i	$a_{i,\varepsilon}$	$b_{i,\varepsilon}$ (K)	$c_{i,\varepsilon}$ (K ²)
Cations				
Im (+)	1	-3.395	-2.203	-20.04
Substituents				
(ring)-H	3	0.768	0.239	-1.863
-CH ₃	2	-0.916	14.681	-32.162
-CH ₂ -	1	-0.261	0.818	-2.914
Anions				
[eFAP] ⁻	1	2.392	-8.346	16.376

$$A_\varepsilon = \sum_{i=1}^k n_i a_{i,\varepsilon} = (-3.395) + (0.768 \times 3) + (-0.916 \times 2) + (-0.261) + 2.392 = -0.792$$

$$B_\varepsilon = \sum_{i=1}^k n_i b_{i,\varepsilon} = (-2.203) + (0.239 \times 3) + (14.681 \times 2) + 0.818 + (-8.346) = 20.348$$

$$C_\varepsilon = \sum_{i=1}^k n_i c_{i,\varepsilon} = (-20.04) + (-1.863 \times 3) + (-32.162 \times 2) + (-2.914) + 16.376 = -76.491$$

$$\varepsilon = \exp\left(A_\varepsilon + B_\varepsilon \frac{100}{T} + C_\varepsilon \left(\frac{100}{T}\right)^2\right) * R_{0\varepsilon} = \left((-0.792) + 20.348 \times \frac{100}{298.15} + (-76.491) \times \left(\frac{100}{298.15}\right)^2\right) \times 7.175$$

$$= 0.548 \text{ S} \cdot \text{m}^{-1}$$

Experimental value [78]: $0.539 \text{ S} \cdot \text{m}^{-1}$

RD(%): 1.67%