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Metal-Containing Ionic Liquids: Anion and Cation Contribution on Thermo-Physical Parameters

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Continuing the researcher's success on ionic liquids application in biomedicine, lithium-sodium batteries, and chemical engineering, we try to investigate temperature, cation, and anion contribution in the most important thermodynamic parameters of the 33 metal-containing ionic liquids. Critical parameters, density, thermal expansion coefficient, critical compressibility factor, surface tension, and lattice energy of studied systems carried out based on classical thermodynamic methods and compared by reported experimental data in the literature. Results revealed that 1-hexyl-3-methyl-imidazolium as cation, and tungsten hepta fluoride as anion show a higher contribution in the boiling temperature (T_b) value; in contrast, hepta-chlorodialuminate as anion, and 1-hexyl-3-methyl-imidazolium as cation showed the main contribution in Vc (critical volume) respectively. The effect of temperature on density has been determined obviously by the first-order polynomial and the proposed method in the present work. 3D graph of surface tension as a function of cation, and anion structure determined the anion group showed the vital influence in surface tension at constant temperature due to the greater polarizability, the lower hydration, and consequently screening the electrostatic repulsion between ionic liquid head groups. Undoubtedly, the provided information in this research is an important help to scientists in choosing the appropriate ionic liquid in specific conditions.

Keywords: Prediction, Anion effect, Metal ionic liquid, Density, Lattice energy, Acentric factor

INTRODUCTION

Developing an effective multi-function ionic liquid (IL) for biomedical applications, dehumidification, bioelectronics, photocatalytic, catalytic, and chemical engineering is an interesting challenge [1-6]. Unique structural characteristics such as high boiling point, electrical, heat conductivity, and selective solubility in organic-inorganic solvents, have promoted high consideration of ILs as green solvents [7], catalysis [8], dispersing agent [9], co-solvent [10], and storage media [11]. Designing and engineering the structure of ILs can target new intrinsic properties, functionality, or environmental safety [12].

Transition metal-containing ILs with remarkable properties in luminescence, gas detection, and magnetism, can decrease the challenge in the stability of ILs in the new conditions [13]. Two methods have been considered for improving the properties of MILs: modification of the hydrocarbon chain length, and counter anion composition. These strategies are also enhancing and optimizing the thermodynamic parameters of metal ILs, like critical parameters, viscosity, density, solubility, vaporization enthalpy, and lattice energy. Determining the structural effect on thermo-physical properties needs a lot of time, and is costly [14-17].

Herein, the impact of temperature, and structure of a new category of ILs in the lattice energy, thermal expansion coefficient, acentric factor, surface tension, and density are established through the prediction of critical parameters of components. Critical pressure, volume, and temperature are obtained by considering the contributions of predetermined

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functional parts, considering the number of each group in the molecule [18-23].

The average free volume model, density functional theory, response surface methodology, new QSPR models, machine-learning model**,** and Monte Carlo are the famous model to predict, and correlate, thermodynamic parameters of ILs [24-28]. The present work would also aim to extrapolate the new method for the coefficient of thermal expansion based on critical parameters. The average relative standard error of the proposed models and the experimental data confirmed the model efficiency in the prediction of thermo-physical properties at different temperatures, and chain lengths. It revealed the metal-containing ILs with $[WF_7]$ and $[AlCl_4]$ anion present the highest and lowest density, respectively. The variation rate of thermodynamic parameters as a function of temperature, cation, and anion structure confirmed the influential role of these parameters. The calculated lattice energy is close to the lattice energy of usual ILs, which is less than that of ionic salts. Also increasing the size of anion showed a reducing efficacy in the lattice energy of ILs due to the decrease of the columbic interaction between ions. Based on obtained results, we propose that the metal-containing ILs showed special physical properties in comparison with usual ILs.

THEORETICAL CALCULATIONS

The Modified Group Contribution approach presented by Lydersen is mainly used to determine critical parameters of materials [29]. In continuation, Joback and Reid displayed a similar model to consider the new condition [30]. In this model, the thermodynamic parameter of chemical compounds is extrapolated by considering contribution and the number of groups, respectively, without assuming interaction between groups and molecules. Fast and simple estimation without requiring complex computational calculations is the best advantage of this method.

Alvarez and Valderrama [31] utilize the Lydersen`s and Joback-Reid models to obtain a "*Modified Lydersen-Joback-Reid*" model that improved the calculated results of heavy molecules.

Valderrama *et al.* [32-34] have recently continued the estimation of the critical parameters of ILs based on the "*Modified Lydersen-Joback-Reid*." Due to the instability of ILs in the high temperature; the accuracy of the method, was studied by density values.

Valderrama *et al.* modified the suggested group contribution model in 2019 to calculate the critical parameters of metal-containing ILs similar to the free metal ionic only by adding a particular value to a given property [35]

In the present work, we try to calculate density, surface tension, acentric factor, lattice energy, thermal expansion coefficient, and compressibility factor of 33 pure MIL at different temperatures in accordance with Eq. (1).

$$\rho = \frac{\acute{A}}{B} + \frac{2}{7}\left(Aln\frac{B}{\acute{B}}\right)\frac{(T-T_C)}{(T_C-T_B)} \quad (1)$$

Where

$$A = a + \frac{bM}{V_C} \quad (2)$$

$$\acute{B} = \left(\frac{c}{V_c} + \frac{d}{M}\right)V_c^b \quad (3)$$

$$V_C\left(\frac{cm^3}{mol}\right) = D + \sum n\Delta V_c \quad (4)$$

$$T_b(K) = 198.2 + \sum n\Delta T_b \quad (5)$$

$$T_c(K) = \frac{T_b}{A + B\sum n\Delta T_c - (\sum n\Delta T_c)^2} \quad (6)$$

$(A = 0.5703\ \ B = 1.0121$ and $D = 6.75)$

$a = 0.3411\ \ b = 2.0443\ \ c = 0.5386$ and $d = 0.02111$

Where T_c, and T_b represent the critical and boiling temperatures respectively, *M* shows molecular weight, and V_C reveals the critical volume of materials. n Shows the number of the main group, $\Delta V_c, \Delta T_b, \Delta T_c$ reveal critical volume, boiling temperature, and critical temperature, respectively [22,36,37]. Table 1 gives the calculated critical parameters of 33 MILs.

Table 2 also shows values of calculated density, critical compressibility factor, and acentric factor by using Eqs. (1), (7), and (8).

$$\omega = \left[\frac{(T_b-43)}{(T_C-T_B)}\frac{(T_c-43)}{(0.7T_c-43)} - \frac{(T_c-43)}{(T_c-T_B)} + 1\right]\log\left[\frac{P_C}{P_b}\right] - 1 \quad (7)$$

$$P_b = 1.01325\ bar$$

$$Z_C = \frac{P_C V_C}{R T_C} \quad (8)$$

In general, the thermal expansion coefficient at constant pressure could be extracted from the density *versus* temperature graph. Herein an equation based on the group

Table 1. Calculated Critical Parameters of the Studied MILs

IL	T_b (K)	T_c (K)	V_c ($cm^3\ mol^{-1}$)	Pc (bar)
[Emim][Al_2Cl_7]	786.15	1080.65	1020.85	36.38
[Emim][$AlCl_4$]	649.21	924.30	737.69	34.97
[Mmim][$AlCl_4$]	626.33	906.51	680.58	38.95
[Prmim][$AlCl_4$]	672.09	935.45	794.80	36.71
[Bmim][$AlCl_4$]	694.97	946.10	851.91	33.15
[Pmim][$AlCl_4$]	717.85	956.30	909.02	30.27
[Hmim][$AlCl_4$]	740.73	966.07	966.13	27.81
[Bmim][$InCl_4$]	889.54	1213.31	903.75	42.37
[Mmim][$InCl_4$]	820.90	1190.66	732.42	63.05
[Emim][$InCl_4$]	843.78	1203.74	831.68	54.35
[Prmim][$InCl_4$]	866.66	1217.26	888.79	48.32
[Pmim][$InCl_4$]	912.42	1217.79	960.86	38.40
[Hmim][$InCl_4$]	935.30	1222.08	1017.97	34.98
[Hmim][$GaCl_4$]	834.35	1090.28	982.56	31.36
[Emim][$GaCl_4$]	742.83	1059.83	754.12	46.95
[Bmim][$GaCl_4$]	788.59	1075.72	868.34	37.76
[Pmim][$GaCl_4$]	811.47	1083.16	925.45	34.29
[C_4Py][Al_2Cl_7]	793.63	961.50	1128.19	30.72
[Bmim][Zn_3Cl_7]	1467.81	2676.56	1278.06	34.82
[Bmim][Zn_2Cl_5]	1164.55	1945.08	1003.55	26.71
[Emim][$FeCl_4$]	681.20	930.30	783.77	34.06
[Bmim][$FeCl_4$]	780.20	1095.80	897.99	35.88
[Emim] [$MoOF_5$]	671.00	920.10	752.60	37.20
[Emim]WOF_5]	959.80	1335.20	705.90	48.70
[S111][Al_2Br_7]	899.72	1349.10	1121.90	28.10
[S111][Al_2Cl_6Br]	727.22	1044.70	1034.78	49.65
[S111][Al_2Cl_7]	698.47	996.84	1020.26	55.56
[Emim] [NbF_6]	728.96	1028.48	748.00	40.79
[Emim][SbF_6]	793.96	1241.78	689.70	43.98
[Emim][TaF_6]	613.96	969.91	763.11	51.25
[Emim][WoF_5]	959.41	1346.40	794.87	40.07
[Emim][WF_7]	936.93	1325.00	747.67	52.06
[Bmim][$Au(CN)_2$]	1172.54	1579.26	868.67	70.88

contribution method and critical parameters has been introduced to determine the thermal expansion coefficient of MIL`s. Equation (10) show the calculation of the thermal expansion coefficient based on the critical parameters without applying density at different temperature. Calculated α for studied systems was given in Table 2.

$$\alpha = (\frac{\partial ln\rho}{\partial T})_P \tag{9}$$

$$\alpha = (\frac{\partial ln\rho}{\partial T})_P = \left[\frac{\partial \ln\left(\frac{\acute{A}}{B}+\frac{2}{7}\left(Aln\frac{B}{B}\right)\frac{(T-T_C)}{(T_C-T_B)}\right)}{\partial T}\right]_P = \left[\frac{\frac{2}{7}\left(Aln\frac{B}{B}\right)\frac{1}{(T_C-T_B)}}{\frac{\acute{A}}{B}+\frac{2}{7}\left(Aln\frac{B}{B}\right)\frac{(T-T_C)}{(T_C-T_B)}}\right]_P \tag{10}$$

In the next step, the corresponding-states group-contribution model (CSGC) is used to calculate the surface tension of MIL. This method was proposed by Brock and Bird (BBT) based on critical parameters of components [37-39]. Equations (11)-(14) display the calculation of surface tension, respectively.

$$\sigma = \left(\frac{P_c}{101.325}\right)^a (T_c)^b (c\alpha - d)(1 - T_r^*)^e \tag{11}$$

$$\alpha = f\left(1 + \frac{T_{br}^* \, ln\,(\frac{P_C^*}{101.325}}{1-T_{br}^*}\right) \tag{12}$$

Where

$$T_r^* = \frac{T}{T_c} \tag{13}$$

$$T_{br}^* = \frac{T_b}{T_c} \tag{14}$$

Table 2 gives obtained surface tension for studied MIL at different chain lengths, and structures.

The lattice energy (LE) of IL is calculated by Glasser's model based on the following equation [40].

$$U_{POT} = 198.2\,[\rho/_M]^{1/3} \tag{15}$$

The values of lattice energy for studied ILs were calculated based on Eq. (15) and reported in Table 2.

RESULTS AND DISCUSSION

T_c, T_b, and V_C, of MILs in the present research using Eqs. (2)-(6) are given in Table 1. Since real parameters of metal ILs do not report the "accuracy" of the calculated parameters estimated by density values. The reliability of this model mainly depends on the availability of data for all functional groups. The model will lead to considered deviation when the method is applied to the calculation of other systems.

Anion and cation contribution in total values of critical boiling temperature and critical volume also extrapolated and showed in Fig. 1. Accordance to the results in Fig. 1a [Emim] and [Bmim] cations showed the most significant effect on the total amount of boiling temperature for [Emim][TaF_6] and [Bmim] [$Au(CN)_2$] ILs. Values of critical parameters were used to calculate density respectively. The density of the studied system is shown in Table 2 as typical (All of the determined parameters are reported in Table S1 in supporting materials).

To compare calculated and experimental data, the standard error was obtained for ILs system and, reported in Table 3, and S2. The values show an acceptable trend with the literature data and confirm the efficiency of the applied model to predict density of metal-containing ILs as a function of temperature.

$$AAD\% = 100 \times \left[\frac{1}{N_P}\sum_i \left(\frac{\sigma_{i,\exp} - \sigma_{i,cal}}{\sigma_{i,\exp}}\right)^2\right]^{1/2} \tag{16}$$

Table S2 shows uncertainties of density and surface tension, standard deviations, and average absolute deviations (AAD) for studied metal ILs in the present work**.** Unfortunately, limited papers have been devoted to report the density and surface tension of metal-containing ILs. In the present research, the surface tension and density of ILs have been predicted with acceptable relative errors. The observed deviation may be due to the intrinsic deviation of the applied model.

The calculated density and surface tension of the studied systems were reduced with rising temperature. In general, the densities of compounds decrease as a function of temperature, which determines that the volume of materials

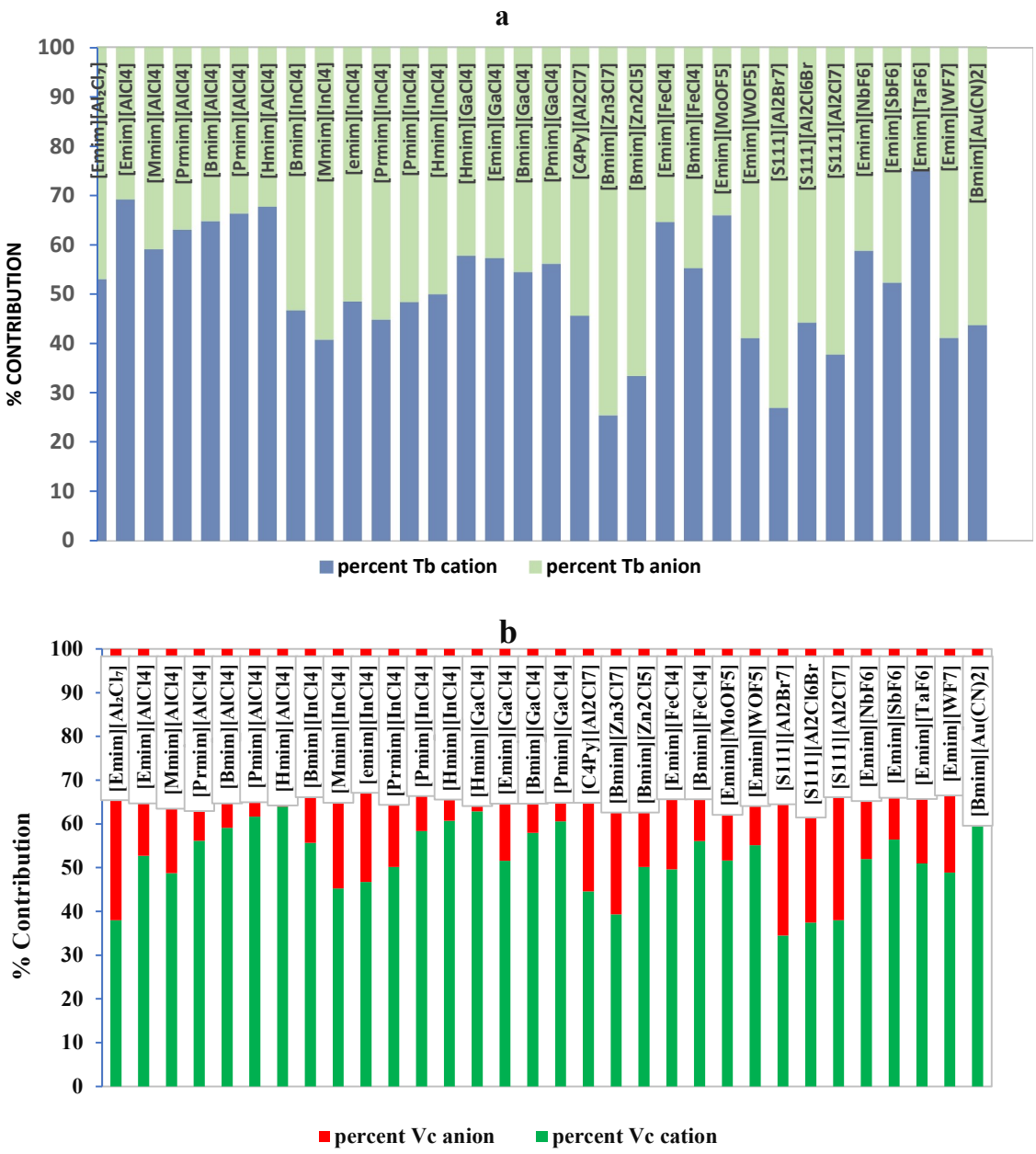

Fig. 1. Cation and anion % contribution in the total value of (a) boiling temperature T_b and (b) critical volume, Vc

enhanced during temperature increasing, and mass per unit volume ratio reduced [51]. In all of the studied systems, the first-order polynomial model with correlation coefficients between 0.9-1 described the relation between density and temperature. The second term in Eq. (1) was used in extracting the thermal expansion coefficient and showing the dependence of temperature changes on the volume of different ILs.

Among the mentioned ILs in Table 2, the highest thermal expansion coefficient value was observed for $[C_4Py][Al_2Cl_7]$. The thermal expansion coefficient is lower than other organic salts and higher than organic compounds. It is clear that the thermodynamic parameters of ILs varied by structure of anion, and cation. The structure of an IL directly affects intermolecular interaction and physical properties in particular the density, surface tension, and viscosity.

Table 2. Calculated Values of Surface Tension, Density, Coefficient of Thermal Expansion, Compressibility Factor, Acentric Factor, and Lattice Energy of the Studied MILs

IL	T (K)	ρ (g cm^{-3})	σ_{cal} (mN m^{-1})	α (K^{-1})	U (kJ mol^{-1})	ω	Z
[Emim][Al_2Cl_7]	293.15	1.3833	53.95	7.26E-05	302.11	0.79	0.41
[Mmim][$AlCl_4$]	298.15	1.2621	57.35	5.37E-05	338.90	0.52	0.35
[Emim][$AlCl_4$]	283.15	1.2503	53.51	5.78E-05	332.19	0.56	0.34
[Prmim][$AlCl_4$]	298.15	1.2420	48.35	6.44E-05	326.16	0.71	0.38
[Bmim][$AlCl_4$]	298.15	1.2383	42.48	7.14E-05	320.88	0.81	0.36
[Pmim][$AlCl_4$]	298.15	1.2373	40.22	7.91E-05	316.12	0.92	0.35
[Hmim][$AlCl_4$]	283.15	1.2389	40.29	8.74E-05	311.85	1.05	0.34
[Mmim][$InCl_4$]	298.15	1.5959	57.03	3.90E-05	322.48	0.67	0.45
[Emim][$InCl_4$]	293.15	1.4662	51.20	4.45E-05	313.59	0.74	0.45
[Prmim][$InCl_4$]	298.15	1.4606	46.67	5.12E-05	304.95	0.79	0.43
[Bmim][$InCl_4$]	283.15	1.4025	41.91	4.95E-05	307.98	0.92	0.38
[Pmim][$InCl_4$]	298.15	1.3953	42.74	5.56E-05	303.73	1.04	0.37
[Hmim][$InCl_4$]	288.15	1.3915	44.87	6.21E-05	300.11	1.17	0.35
[Mmim][$GaCl_4$]	298.15	1.3537	34.65	4.74E-05	325.37	0.68	0.40
[Bmim][$GaCl_4$]	298.15	1.3316	33.81	5.92E-05	314.85	0.86	0.37
[Pmim][$GaCl_4$]	298.15	1.3258	33.92	6.59E-05	310.37	0.97	0.35
[Hmim][$GaCl_4$]	283.15	1.3255	32.48	7.32E-05	306.51	1.10	0.34
[C_4Py][Al_2Cl_7]	298.15	1.4771	27.56	1.58E-04	302.71	2.04	0.43
[Bmim][Zn_3Cl_7]	318.2	1.2562	63.97	6.30E-07	261.19	0.32	0.22
[Bmim][Zn_2Cl_5]	313.15	1.2262	41.76	4.37E-07	282.95	0.90	0.16
[Emim][$FeCl_4$]	293.15	1.3182	31.31	7.46E-05	327.57	0.84	0.38
[Bmim][$FeCl_4$]	298.15	0.9694	35.41	3.85E-05	295.98	0.65	0.45
[Emim][$MoOF_5$]	298.15	1.4008	30.70	7.99E-05	330.70	0.82	0.37
[Emim][WOF_5]	298.15	1.6751	53.48	3.51E-05	323.63	0.85	0.31
[S111][Al_2Br_7]	298.15	1.9513	34.73	5.88E-05	285.57	0.24	0.28
[S111][Al_2Cl_6Br]	298.15	1.4011	43.92	7.30E-05	300.77	0.66	0.59
[S111][Al2Cl7]	298.15	1.2954	45.93	7.35E-05	304.01	0.75	0.69
[Emim][NbF_6]	298.15	1.3563	36.97	5.25E-05	327.19	0.68	0.36
[Emim][SbF_6]	298.15	1.4617	46.47	2.43E-05	326.12	0.24	0.29
[Emim][TaF_6]	298.15	1.6828	41.89	6.87E-05	324.35	0.25	0.49
[Emim][WoF_5]	298.15	1.5201	46.06	3.30E-05	313.65	0.70	0.29
[Emim][WF_7]	298.15	1.5333	56.07	3.13E-05	318.76	0.78	0.35
[Bmim][$Au(CN)_2$]	298.15	1.2830	81.93	1.13E-05	300.76	1.29	0.47

Variation in these characteristics validates ILs in different industries and research areas. The volume and molecular weight of ions are essential factors that influence the density of the compounds [39].

Results in Fig. 2 show the obvious variation of ρ as a function of different anions for a special cation. In the studied

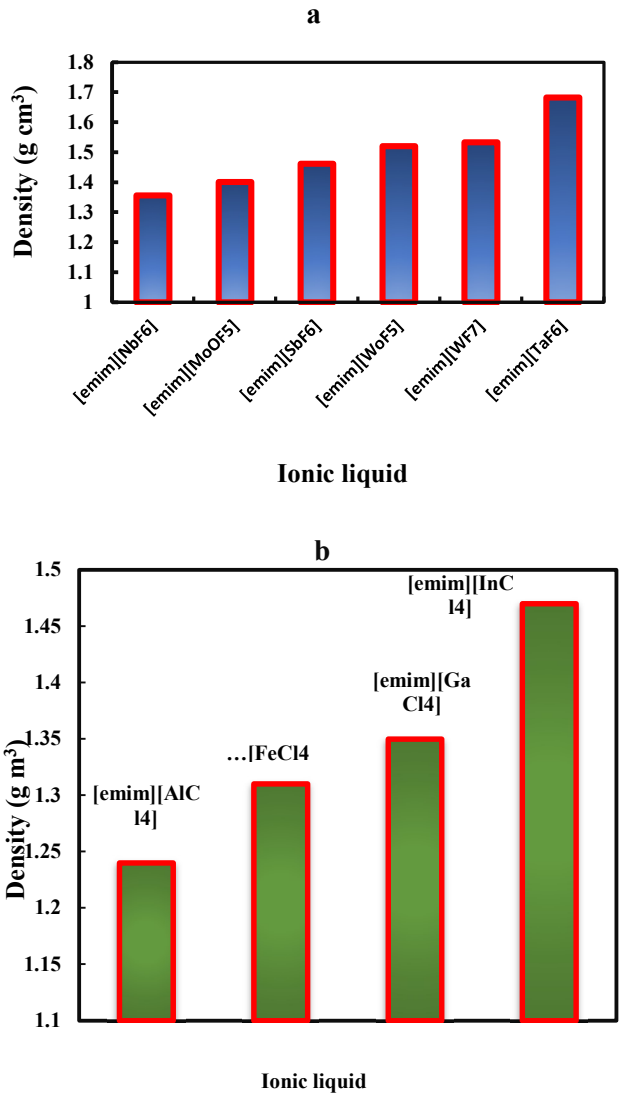

Fig. 2. Variation of density as a function of different (a) cation, and (b) anion.

systems metal containing ILs containing [WF_7] anion show the highest density, while the replacement of anion with the [$AlCl_4$] ion decreases the density. It was determined that the anion showed a significant influence on the ILs density, and the density increased with the "molecular weight" of the anions for a constant cation, *i.e.* in the order [$AlCl_4$] < [$FeCl_4$] < [$GaCl_4$] < [$InCl_4$] for the [MCl_4] series and [NbF_6] <[$MoOF_5$] < [SbF_6] < [TaF_6] < [WF_7] for the [MFx] series of IL respectively (see Fig. 2) [52,53]

The separation between ions could be the result of the interactions between ions, effectively generated by electrostatic force, geometrical shape, polarization ability, and weak forces of ions (*i.e.*, hydrogen bond), many unknown parameters. This behavior was also reported for other series ILs in the literature confirming that the group contribution method has a good efficiency [54,55].

According to Table 2, it revealed that IL density decreased whit increasing the hydrocarbon chain length of the imidazolium due to the enhanced occupied total volume by the cations. Actually, this result originates from the enhancing anion-cation dissociation and the decreasing packing order and density respectively. In general, the increase of alkyl chains has a clear effect on the IL's density. A similar trend has been observed in literature for densities in the homologous series [56-58]. An increase in the number of CH_2 groups in saturated hydrocarbons generates an increase in density, due to the progressive compact of the alkyl chains via van der Waals forces. Also, Filippov *et al.* showed at the ambient condition the densities of the general ILs are substantial than aliphatic compounds [59].

ILs generally composed of a cyclic imidazole cation and a small inorganic anion. This existence asymmetrical decreases the lattice energy of the crystalline network in comparison with salts.

From Table 2, it revealed that the lattice energies of studied MILs are between 257-327 kJ mol^{-1}. 257 kJ mol^{-1} for [Bmim][Zn_3Cl_7] which has the least lattice energy between studied MILs however, the most significant value for [Mmim][$AlCl_4$] is 341 kJ mol^{-1} due to the more asymmetry in structure. As shown in Table 1 temperature, metal kind, and chain length affect the lattice energy of ILs. Lattice energy decreased via temperature enhancement. In this equation, density decreased as a function of temperature and so lattice energy decreased [60,61].

As shown in Table 2, Lattice energy decreased when side chain length and molecular volume increased for the [$M_n$mim][$Alcl_4$] series. This behavior was confirmed by reported ab initio quantum mechanical results in the literature, which showed a reduction in interaction energy by adding hydrocarbon chain length at the Hartree-Fock model [56]. The obtained values in Table 2 also showed lattice energy changes also with the change of metal in anion structure and temperature in the same ILs. Lattice energy is reduced with the rising temperature due to the decreasing hard-sphere intermolecular potential. In addition, at high

Table 3. Deviations in Density and Surface Tension Calculation for Studied Metal ILs in the Present Work

IL	T/K	%Δρ	%Δσ	Ref.
[Emim][Al_2Cl_7]	293	0.8565		[41]
[Mmim][$AlCl_4$]	298	0.0350	0.5164	[42]
[Emim][$AlCl_4$]	283.15	0.1817	1.0511	[42]
[Prmim][$AlCl_4$]	298.15	0.0307	0.2867	[42]
[Bmim][$AlCl_4$]	298.15	0.0000	0.4539	[42]
[Pmim][$AlCl_4$]	298.15	0.0392	0.4692	[42]
[Hmim][$AlCl_4$]	283.15	0.0722	0.1907	[41]
[Emim][$InCl_4$]	293.15	1.1376	1.4244	[43]
[Prmim][$InCl_4$]	298.15	0.6732	-	[43]
[Bmim][$InCl_4$]	283.15	1.2197	-	[44]
[Pmim][$InCl_4$]	298.15	0.5844	-	[42]
[Hmim][$InCl_4$]	288.15	0.4133	0.1373	[42]
[Emim][$GaCl_4$]	298.15	0.6716	1.1836	[45]
[Bmim][$GaCl_4$]	298.15	0.3664	1.0374	[45]
[Pmim][$GaCl_4$]	298.15	0.1308	0.8913	[45]
[Hmim][$GaCl_4$]	283.15	0.0601	0.4959	[45]
[C_4Py][Al_2Cl_7]	298.15	1.0357		[46]
[Bmim][Zn_3Cl_7]	318.2	8.6368	1.5328	[47]
[Bmim][Zn_2Cl_5]	313.15	8.6017	0.0740	[48]
[Emim][$FeCl_4$]	293.15	0.5142	0.1832	[49]
[Bmim][$FeCl_4$]	298.15	0.4226	-	[49]
[Emim][$MoOF_5$]	298.15	4.1647	0.3772	[50]
[Emim][WOF_5]	298.15	6.5288	-	[50]
[S111][Al_2Br_7]	298.15	3.4950	-	[50]
[S111][Al_2Cl_6Br]	298.15	1.4122	-	[50]
[S111][Al_2Cl_7]	298.15	0.5579	-	[50]
[Emim][NbF_6]	298.15	3.5277	-	[51]
[Emim][SbF_6]	298.15	4.4065	-	[51]
[Emim][TaF_6]	298.15	5.0414	-	[51]
[Emim][WF_7]	298.15	10.5311	-	[52]
[Bmim][$Au(CN)_2$]	298.15	9.8552	1.7865	[49]

temperature, the molecules moved more quickly, so the dispersive force and polar interaction effect in the compressibility factor decreased. However, the ionic force expressed an effective contribution in the compressibility factor in comparison with the wander Waals attraction.

CONCLUSION

In the present paper, the Modified Group Contribution model is used to predict the coefficient of thermal expansion, compressibility factor, acentric factor, and lattice energy of

metal-containing ILs prediction could be successfully extended. The presented strategy lets us surface tension of MILs at different conditions predict. The effectiveness of the model was determined by evaluating the thermodynamic parameters of MIL. Calculated physical parameters are in good consistent with real values at different temperatures, anions, and chain lengths. It is concluded that the suggested method can also be applied to predict the lattice energy, acentric factor, and compressibility factor of different ILs. It determined that the ion structure showed an impressive influence on the predicted physical properties.

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Nomenclature

[Emim][Al_2Cl_7] heptachlorodialuminate	1-Ethyl-3-methylimidazolium
[Mmim][$AlCl_4$] chloroaluminate	1-Methyl-3-methylimidazolium
[Emim][$AlCl_4$] chloroaluminate	1-Ethyl-3-methylimidazolium
[Prmim][$AlCl_4$] chloroaluminate	1-Propyl-3-methylimidazolium
[Bmim][$AlCl_4$] chloroaluminate	1-Buthyl-3-methylimidazolium
[Pmim][$AlCl_4$] chloroaluminate	1-Penthyl-3-methylimidazolium
[Hmim][$AlCl_4$] chloroaluminate	1-Hexyl-3-methylimidazolium
[Mmim][$InCl_4$] chloroindium	1-Methyl-3-hexylimidazolium
[Emim][$InCl_4$] chloroindium	1-Ethyl-3-hexylimidazolium
[Prmim][$InCl_4$] chloroindium	1-Methyl-3-hexylimidazolium
[Bmim][$InCl_4$] chloroindium	1-Butyl-3-methylimidazolium
[Pmim][$InCl_4$] chloroindium	1-Pentyl-3-methylimidazolium
[Hmim][$InCl_4$] chloroindium	1-Hexyl-3-methylimidazolium
[Emim][$GaCl_4$] chlorogallate	1-Ethyl-3-hexylimidazolium
[Bmim][$GaCl_4$] chlorogallate	1-Buthyl-3-hexylimidazolium
[Pmim][$GaCl_4$] chlorogallate	1-Penthyl-3-hexylimidazolium
[Hmim][$GaCl_4$] chlorogallate	1-Hexyl-3-hexylimidazolium
[C_4Py][Al_2Cl_7] heptachlorodialuminate	Butylpyridinium
[Bmim][Zn_3Cl_7] heptachloro zincate	1-Butyl-3-methylimidazolium
[Bmim][Zn_2Cl_5] pentachloro zincate	1-Butyl-3-methylimidazolium
[Emim][$FeCl_4$] tetrachloroferrate	1-Ethyl-3-methylimidazolium
[Bmim][$FeCl_4$] tetrachloroferrate	1-Buthyl-3-methylimidazolium
[Emim][$MoOF_5$] oxopentafluoromolybdate	1-Ethyl-3-methylimidazolium
[Emim][WOF_5] oxypentafluorotungstate	1-Ethyl-3-methylimidazolium
[S111][Al_2Br_7] heptabromodialuminate	Trimethylsulfonium
[S111][Al_2Cl_6Br] hexachlorobromodialuminate	Trimethylsulfonium
[S111][Al_2Cl_7] heptachlorodialuminate	Trimethylsulfonium
[Emim][NbF_6] hexafluoroniobium	1-Ethyl-3-methylimidazolium
[Emim][SbF_6] hexafluoroantimonate	1-Ethyl-3-methylimidazolium
[Emim][TaF_6] hexafluorotantalum	1-Ethyl-3-methylimidazolium
[Emim][WF_7] heptafluorotungstate	1-Ethyl-3-methylimidazolium
[Bmim][$Au(CN)_2$] dicyanoaurate	1-Butyl-3-methylimidazolium

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