COMPARISON OF GROUP CONTRIBUTION METHODS FOR IONIC LIQUIDS

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Abstract: Ionic liquids (ILs) stand out as a possible green substitute for the conventional solvents due to their characteristics such as low vapor pressure, versatility, and chemical stability. However, experimental studies are still expensive and molecular simulations demand high computational power. On the other hand, group contribution methods (GCMs) emerge as a viable tool for properties' prediction. In this study, twenty -five ILs were selected, the properties were evaluated and compared using the modified Joback (MJ) and Marrero-Gani (MG) GCMs. The range of application was analyzed, and the accuracy of the calculated specific mass was evaluated using literature. The results show that the MJ method is superior, once it could describe all the selected ILs and with a mean specific mass deviation 10.31 times smaller than MG.

Keywords: group contribution, modified Joback, Marrero-Gani, ionic liquid.

COMPARAÇÃO ENTRE MÉTODOS DE CONTRIBUIÇÃO DE GRUPO PARA LÍQUIDOS IÔNICOS

Resumo: Os líquidos iônicos (ILs) se destacam como um possível substituto verde aos solventes moleculares e pelas suas características como baixa pressão de vapor, versatilidade e estabilidades térmica e química. Entretanto, o estudo experimental de suas propriedades pode ser caro e demandar elevado poder computacional. Assim, os métodos de contribuição de grupo (GCM) surgem como uma ferramenta acessível na predição de propriedades. Foram selecionados vinte e cinco ILs para comparar os GCMs de Joback modificado (MJ) e Marrero-Gani (MG). Foram analisados o range de ação e a precisão da densidade calculada com a literatura. Com isso, o método MJ modificado se mostrou superior, já que foi capaz de descrever todos os ILs e alcançou um desvio médio da densidade 10.31 vezes menor que o MG.

Palavras-chave: contribição de grupo, Joback modificado, Marrero-Gani, líquido iônico.

1. INTRODUCTION

By the modern definition, ILs are salts with melting point below the boiling point of the water (100 ºC). Commonly, their molecular structure has a voluminous organic cation and small sized anion. In addition, they have some particular characteristics such as: negligible vapor pressures, great versatility, and high thermochemical stability. Their versatility comes from the possibility of modifying their anion and cation to achieve the desired physicochemical properties [1].

The first research to present a substance with such properties was carried out by Paul Walden in 1914 [2]. He synthesized a liquid salt, ethylammonium nitrate ($[EtNH_3][NO_3]$), with a melting point of 12 ºC. Following this discovery, by the modern definition, the $[EtNH_3][NO_3]$ is characterized as a IL. Furthermore, later, at the end of 20^{th} century, the substances in the group of ILs were pointed as a potential alternative to common molecular solvents in chemical processes. Moreover, the creation of a green chemical concept resulted in a sharp increase in the number of published works about ILs [2,3].

Despite the current increase on the topic of ILs, there are still some challenges related to the high cost to synthesize some kinds of ILs or to perform complex molecular simulations which requires high computational resources. Therefore, to circumvent these problems, some alternatives to study the possible applications and properties of ILs have been proposed.

Group contribution methods (GCMs) are commonly used to study and predict the properties of new substances. In this kind of method, those properties are functions of the component structure, where the absolute value of the property is given by an equation that correlates every functional group of the molecule. The advantage of GCM lays on the quick estimates and low computational efforts required. However, limitations like the modest accuracy and the lack of capability to distinguish isomers are presents on these methods [4].

Among the GCMs, the method developed by Marrero-Gani (MG) [4] can predict properties of a broad variety of compounds and is widely used in many engineering software. Another well-known GCM is that proposed by Joback [5], which, for most compounds, has less accuracy than theMG even though needs less computational power. However, in 2009 Valderrama [5] made a modification to the Joback [4] GCM in order to adapt it to predict ILs's properties.

In view of this, the objective of this paper is to compare two GCMs: the Marrero-Gani [4] and the modified Joback (MJ) [5], and to determine which method can better predict the critical properties and the specific mass of ILs.

2. METHODOLOGY

Initially, 25 LIs (Table 2) with a wide range of anions and cations were selected to compare the GCMs modified Joback [5] and Marrero-Gani [4]. After that, the software Microsoft Excel™ was used to perform the calculations of the following properties: boiling and critical temperature, critical volume, and specific mass. The equations in Table 1 were used for the methods.

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Table 1. Method's equations

Modified Joback equations		**Parameters**	
Boiling temperature (K)	$T_b = 198.2 + \sum n \cdot \Delta T_b$	**A**	0.5703
Critical temperature (K)	$T_c = \frac{T_b}{A + B \cdot \sum n \cdot \Delta T_c - (\sum n \cdot \Delta T_c)^2}$	**B**	1.0121
Critical volume (cm³/mol)	$V_c = D + \sum n \cdot \Delta V_c$	**D**	6.75
Marrero-Gani equations		**T_{m0} (K)**	147.45
Boiling temperature (K)	$T_b = T_{b0} \cdot \ln\left(\sum n_i \cdot T_{b1,i} + \sum m_j \cdot T_{b2,j} + \sum o_k \cdot T_{b3,k}\right)$	**T_{c0} (K)**	231.239
Critical temperature (K)	$T_c = T_{c0} \cdot \ln\left(\sum n_i \cdot T_{c1,i} + \sum m_j \cdot T_{c2,j} + \sum o_k \cdot T_{c3,k}\right)$	**P_{c1} (bar)**	5.9827
Critical volume (cm³/mol)	$V_c = V_{c0} + \sum n_i \cdot V_{c1,i} + \sum m_j \cdot V_{c2,j} + \sum o_k \cdot V_{c3,k}$	**V_{c0} (cm³/mol)**	7.95
Specific mass (gm/cm³)			
$\rho = \frac{A_2}{B_2} + \frac{2}{7} \cdot \left(\frac{A_2 \cdot ln(B_2)}{B_2} \cdot \frac{T - T_b}{T_c - T_b}\right)$			
$A_2 = 0.3411 + 2.0433 \cdot \frac{M}{V_c}$	$B_2 = \left(\frac{0.5386}{V_c} + \frac{0.0393}{M}\right) \cdot V_c^{1.0476}$		

Finally, the MJ and MG methods were compared. First, it was verified which ILs molecules could be described by the group contribution in each method. After that, due to the small number of published papers on this topic, that study the critical and energy properties (enthalpy and Gibbs) of ILs experimentally, the specific mass was chosen as the major property for comparison between the two methods. The calculated specific mass was compared with the literature data to establish the average deviation of each method.

3. RESULTS AND DISCUSSION

After the range of each method was analyzed, the results obtained, (Table 2), show that the MJ method has a wider performance range than the MG.

Table 2. GCM range of application comparison.

Ionic Liquid	**Molecular formula**	**Modified Joback**	**Marrero-Gani**
1-Ethyl-3-methylimidazolium tetrafluoroborate	$C_6H_{11}N_2BF_4$	•	-
1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	$C_8H_{11}N_3S_2O_4F_6$	•	-

1-Ethyl-3-methylimidazolium trifluoroacetate	$C_8H_{11}N_2O_2F_3$	●	●
1-Butyl-3-methylimidazolium hexafluorophosphate	$C_8H_{15}N_2PF_6$	●	-
1-Butyl-3-methylimidazolium nitrate	$C_8H_{15}N_3O_3$	●	-
1-Butyl-3-methylimidazolium isobutyrate	$C_{12}H_{22}N_2O_2$	●	●
1-Butyl-3-methylimidazolium taurate	$C_{10}H_{21}O_3N_3S$	●	●
1-Butyl-3-methylimidazolium glycinate	$C_{10}H_{19}O_2N_3$	●	●
1-Hexyl-3-methylimidazolium trifluoromethane-sulfonate	$C_{11}H_{19}N_2O_3SF_3$	●	●
1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluoro-phosphate	$C_{16}H_{19}N_2PF_{18}$	●	-
1-Octyl-3-methylimidazolium hexafluorophosphate	$C_{12}H_{23}N_2PF_6$	●	-
Bis(1-butyl-3-methylimidazolium) iminodiacetate	$C_{20}H_{35}N_5O_4$	●	●
Ethanolammonium butyrate	$C_6H_{15}O_3N$	●	-
Bis(2-ethylhexyl) ammonium butyrate	$C_{20}H_{33}O_2N$	●	●
Tributylammonium acetate	$C_{14}H_{31}O_2N$	●	●
N-methyl-2-hydroxyethylammonium formate	$C_4H_{11}NO_3$	●	●
Trihexyltetradecylphosphonium chloride	$C_{32}H_{68}PCl$	●	-
Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide	$C_{34}H_{68}PNS_2O_4F_6$	●	-
1-Butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluoro-phosphate	$C_{15}H_{20}NPF_{18}$	●	-
1-Butyl-3-methylimidazolium tetrafluoroborate	$C_8H_{15}N_2BF_4$	●	-
1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	$C_{10}H_{15}N_3S_2O_4F_6$	●	-
1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	$C_{12}H_{19}N_3S_2O_4F_6$	●	-
1-Octyl-3-methylimidazolium tetrafluoroborate	$C_{12}H_{23}N_2BF_4$	●	-
Ethanolammonium acetate	$C_4H_{11}O_3N$	●	-
1-Butyl-3-methylimidazolium chloride	$C_8H_{15}N_2CL$	●	●

The MJ method was able to represent all selected ILs, whilst, MG represented only 10 out of 25 ILs. This happens due to the fact that MG does not have relevant groups commonly used in LIss, such as: phosphorus, boron and nitrogen in its aliphatic atomic form, nitrate (NO_3) and the CNH group. However, this method performs well on organic cations and anions.

Then, the ILs that could be calculated by both methods were used to check the accuracy of each method in calculating properties. The property used for the comparison between the methods, specific mass (Table 3), is dependent on three other properties (critical and boiling temperature, and critical temperature) which were calculated using the GCMs.

Table 3. Calculated specific mass and deviations.

	Specific mass (g/cm³)				
Ionic liquid	**Literature**	**Modified Joback / Deviation**		**Marrero-Gani / Deviation**	
1-Ethyl-3-methylimidazolium tetrafluoroborate	1.282[6]	1.300	1.42%	-	-
1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	1.518[7]	1.522	0.23%	-	-
1-Ethyl-3-methylimidazolium trifluoroacetate	1.291[8]	1.344	4.07%	2.888	123.71%
1-Butyl-3-methylimidazolium hexafluorophosphate	1.366[9]	1.317	-3.59%	-	-
1-Butyl-3-methylimidazolium nitrate	1.156[10]	1.086	-6.08%	-	-
1-Butyl-3-methylimidazolium isobutyrate	1.074[11]	1.059	-1.36%	0.970	-9.66%
1-Butyl-3-methylimidazolium taurate	1.198[12]	1.135	-5.27%	1.191	-0.59%
1-Butyl-3-methylimidazolium glycinate	1.111[13]	1.109	-0.22%	2.199	97.93%
1-Hexyl-3-methylimidazolium trifluoromethane-sulfonate	1.217[14]	1.243	2.16 %	1.276	4.86%
1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluoro-phosphate	1.557[15]	1.573	-1.25%	-	-
1-Octyl-3-methylimidazolium hexafluorophosphate	1.236[16]	1.217	-1.51%	-	-
Bis(1-butyl-3-methylimidazolium) iminodiacetate	1.075[11]	1.080	0.45%	1.361	26.60%
Ethanolammonium butyrate	1.073[17]	1.177	9.71%		
Bis(2-ethylhexyl) ammonium butyrate	0.870[17]	0.935	7.48%	1.001	15.13%
Tributylammonium acetate	0.912[17]	0.928	1.71%	1.065	16.77%
N-methyl-2-hydroxyethylammonium formate	1.128[18]	1.212	7.42%	1.357	20.30%
Trihexyltetradecylphosphonium chloride	0.890[19]	0.886	-0.40%	-	-
Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide	1.066[20]	1.068	0.16%	-	-
1-Butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluoro-phosphate	1.585[21]	1.555	-1.92%	-	-
1-Butyl-3-methylimidazolium tetrafluoroborate	1.201[22]	1.230	2.45%	-	-
1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	1.436[23]	1.447	0.80%	-	-
1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	1.372[24]	1.389	1.21%	-	-
1-Octyl-3-methylimidazolium tetrafluoroborate	1.104[25]	1.141	3.34%	-	-
Ethanolammonium acetate	1.141[11]	1.268	11.16%	-	-
1-Butyl-3-methylimidazolium chloride	1.081[26]	1.110	2.70 %	1.012	-6.38%

The MJ method showed an average deviation of 3.12% and was superior to the MG method in 9 out of 10 ILs that could be compared. The MG method showed an average deviation of 32.19% and better represented only the IL 1-Butyl-3-methylimidazolium taurate.

Thus, these results demonstrate that the MJ method has a greater capability to describe the ILs molecules. In addition, it has a better accuracy in calculating the specific mass, which makes use of the critical volume and the critical and boiling temperatures.

4. CONCLUSION

The experimental study properties of many ILs can be an expensive process or one that requires high computational power. Thus, GCMs are used as auxiliary methods in predicting these properties.

In this work, the proposed objective was achieved, revealing that the modified Joback method is superior to Marrero-Gani in the study of ILs. In the range analysis, the modified method was able to represent all the ILs tested, while MG was able to represent only 40%. Finally, in the calculation of the specific mass the MJ (3.12% deviation) showed an average deviation 10.31 times lower than the MG method (32.19% deviation).

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