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A review of group contribution models to calculate thermodynamic properties of ionic liquids for process systems engineering

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ABSTRACT

Ionic liquids are compounds with interesting physical and chemical properties that can be applied to a wide variety of processes. The knowledge of their thermodynamic properties is essential for the design of products and processes. These properties include heat capacity, density, viscosity, thermal conductivity, melting point, surface tension, electrical conductivity, refractive index, thermal decomposition temperature, normal boiling point, critical properties, freezing point, isobaric expansivity, isothermal compressibility and static dielectric constant. However, the experimental database available of such properties for ionic liquids is limited, thus affecting the process design and modeling. Different thermodynamic models have been developed to estimate these properties and, group contribution models offer several advantages for these applications. This review covers different group contribution models reported and applied to estimate the thermodynamic properties of ionic liquids. The application, performance, and accuracy of these models for predicting the ionic liquids properties were analyzed and discussed. Some approaches combining group contribution models with artificial neural networks to estimate the thermodynamic properties of ionic liquids have been also described and exemplified. This review offers a survey of a variety of group contribution approaches that can be used to predict several thermodynamic properties of ionic liquids for process systems engineering.

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1. Introduction

Ionic liquids (ILs) are compounds with a low melting point (usually < 100 °C) like conventional salts but composed of organic cations and inorganic or organic anions (Brinchi et al., 2003; Hosseini et al., 2019). Common examples of ILs cations include imidazolium, sulfonium, morpholinium, guanidinium, ammonium, pyridazinium, piperazinium,

oxazolidinium, tetrazolium, morpholinium, uronium, thiazolium, isoquinolinium, pyrroline, piperidinium, pyrrolidinium, pyridinium and phosphonium (Hosseini et al., 2019; Sepehri, 2020). The anions that frequently conform the ILs molecular structure are BF_4^- , PF_6^- , CF_3SO_3^- , $\text{N}(\text{SO}_2\text{CF}_3)_2^-$, SCN^- , R-PO_4^- , R-SO_3^- and R-SO_4^- where R represents an alkyl substituent (Hosseini et al., 2019).

ILs have attractive thermochemical properties for various applications (Feng et al., 2015; Thoms et al., 2017). They are versatile chemicals due to their low vapor pressure, high solubility for polar and non-polar organic and inorganic substances, thermal stability at high temperature, aggregation liquid state at room temperature, low melting

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temperature, besides their reusability, solvation, non-flammable and non-corrosive characteristics (Rooney et al., 2010; Ghandi, 2014; Ayan et al., 2020; Chen et al., 2020; Sepehri, 2020; Bouarab et al., 2021). The physicochemical properties of ILs can be tailored for different processes by varying the cations and anions that conform their molecular structures (Bouarab et al., 2021). Theoretically, it is believed that a vast number of ILs could be synthesized with tuned and enhanced properties for the application at hand (Chen et al., 2019).

To date, ILs have been employed to develop novel processes and products thus contributing to the industry sustainability and circular economy, see Fig. S1 and Table S1 of Supporting Information. One of the most relevant applications of these compounds is as green solvents due to their low vapor pressure that allows to reduce the energy consumption and waste generation in purification and separation units (Wang et al., 2009; Zaid et al., 2017). They can be utilized as an alternative to the well-known volatile organic solvents in the chemical industry to develop environmentally friendly technologies and processes. ILs can dissolve organic and inorganic chemicals (Xiong et al., 2013; Liu et al., 2014; Ayan et al., 2020; Aguilar-Elguezabal et al., 2020), pharmaceuticals (Lee and Lin, 2017), biochemical compounds (Devi et al., 2011; Ortiz-Martínez et al., 2016; Xu et al., 2016; Brogan et al., 2018) and polymeric materials (Valderrama and Robles, 2007; Meksi and Moussa, 2017). For example, Ayan et al. (2020) used ILs for the reactive extraction of propionic acid, while Aguilar-Elguezabal et al. (2020) developed a new process to transform α -pinene into α -terpineol using an IL-based solvent. ILs have been also utilized as extraction agents in distillation processes offering several advantages like a simple recovery, high selectivity and reduction of mass losses (Lei et al., 2014; Qi et al., 2019; Sosa et al., 2020). Qi et al. (2019) evaluated the performance of ethylene glycol and 1,3 - dimethylimidazolium in the extractive distillation of the azeotropic mixture of diisopropyl ether and isopropanol. This IL improved the relative volatility of these compounds and increased the purities obtained from the separation system in comparison to those obtained with ethylene glycol. ILs have also proved to improve the performance of liquid-liquid extraction processes (Marsousi et al., 2019; Sosa et al., 2020; Sommer et al., 2021; Guo et al., 2021). Sosa et al. (2020) evaluated the use of different ILs to separate a mixture of hydrocarbons and ethanol obtaining a better process performance. Guo et al. (2021) carried out a directional solvent extraction with IL for the seawater desalination where a higher water yield was obtained than that generated with the current process using decanoic acid. Another important application of ILs includes catalysis and reaction engineering (Welton, 1999; Adams et al., 2000; Brinchi et al., 2003; Yadav et al., 2003; Irimescu and Kato, 2004; Fukuyama et al., 2007; Arai et al., 2010; Böhm et al., 2014; Lentini et al., 2014; Soares, 2018; Hosseini et al., 2019). Reactive systems with ILs can provide higher activity than their counterparts besides these compounds can facilitate the formation of two phases thus helping the recovery of target compound(s) (e.g., the separation of fatty acid methyl esters during biodiesel production). For instance, Arai et al. (2010) produced biodiesel from soybean oil catalyzed by lipase-producing fungi using four types of imidazolium-based ILs. For interested readers, Vekariya (2017) has reviewed the properties, preparation routes and applications of ILs in catalytic organic transformations. Note that different ILs could show attractive characteristics (e.g., lubricating

properties) to be exploited in diverse industrial applications (Ye et al., 2001; Karmakar and Samanta, 2002; Predel et al., 2009).

The design, simulation and optimization of ILs-based processes require a reliable thermodynamic modeling. The experimental and theoretical characterization of the thermodynamic properties of ILs (e.g., heat capacity, density, viscosity, thermal conductivity, melting point, surface tension, electrical conductivity, refractive index, thermal decomposition temperature, normal boiling point, critical properties, freezing point, isobaric expansivity, isothermal compressibility, static dielectric constant) is crucial for the process systems engineering. The availability of a comprehensive database of ILs thermodynamic properties allows to improve the operating conditions, to develop new sustainable processes and products, to reduce the energy requirements, to avoid the equipment oversizing, to enhance other process performance metrics, and to validate theories and models. Consequently, it is fundamental to carry out experimental studies on the quantification of these properties with the aim of supporting the development of a reliable thermodynamic framework for the calculation, as accurately as possible, of ILs physicochemical behavior. Reliable estimations of ILs thermodynamic properties are required to face and handle the different tasks involved in the process design and simulation. However, the experimental data reported for ILs thermodynamic properties are still scarce and some of them could be inconsistent or uncertain due to noise, determination errors and undetected failures in equipment and/or laboratory procedures. Due to the large number of ILs that can be synthesized for a particular application (e.g., it has been estimated that $\sim 10^6$ possible ionic liquids can be synthesized), it could be complex, expensive and time-consuming to quantify experimentally the properties of all these compounds. The development of reliable predictive thermodynamic models to calculate the physicochemical properties of ILs is paramount for process systems engineering.

Thermodynamic models for the estimation of ILs physicochemical properties include group contribution (GCMs) (Aguirre et al., 2012; Lazzús, 2012a, 2012b; Nancarrow et al., 2015; Sattari et al., 2016a; Lazzús et al., 2017b; Shahsavari et al., 2018; Hosseini et al., 2019; Bouarab et al., 2021), quantitative structure property relationships (QSPR) (El-Harbawi et al., 2014; Hosseini et al., 2019; Sepehri, 2020; Bouarab et al., 2021), artificial neural networks (ANN) (Valderrama et al., 2011a, 2014; Hosseini et al., 2019; Yusuf et al., 2021), least square support vector machine (LSSVM) (Yusuf et al., 2021), equations of state (EoS) (Gadamsetty et al., 2011; Hosseini et al., 2019), molecular dynamics (MD), Monte Carlo (MC) simulations (Vega et al., 2010; Wang et al., 2014; Weiss, 2015; Hosseini et al., 2019) and their variants and hybrid approaches (Deetlefs et al., 2006; Matsuda et al., 2007; Lazzús, 2010b; Valderrama and Rojas, 2010; Vega et al., 2010; Shen et al., 2011; Valderrama et al., 2011b, 2017; Chen et al., 2013; Wu et al., 2014; Farzi and Esmaeilzadeh, 2016; Wang et al., 2017; Hosseini et al., 2019; Bouarab et al., 2021). Fig. S2 provides an overview of these modeling tools. The characteristics, limitations and capabilities of these models can vary substantially depending on the ILs molecular structure and thermodynamic property to be analyzed. However, GCMs stand out as effective and widely used approach to estimate the thermodynamic behavior of ILs (Hosseini et al., 2019; Chen et al., 2019).

GCMs offer advantages for the prediction of ILs thermodynamic properties. These models are characterized by their acceptable accuracy without requiring substantial computational efforts and complex calculations, versatility, straightforward and easy implementation for a broad spectrum of compounds where the knowledge of their molecular structures is usually the input information (Valderrama and Robles, 2007). These models assume that the properties of a compound are a function of its molecular structural elements and tested operating conditions. GCMs can be utilized as thermodynamic models for the process systems engineering involving ILs (Valderrama et al., 2012; Hosseini et al., 2019). However, it is convenient to indicate that the main issue that can affect the use and implementation of GCMs for the prediction of ILs thermodynamic properties is the relatively limited amount of experimental data in comparison with the information contained in the thermodynamic database of traditional chemical compounds. Despite this fact, GCMs are still considered as a straightforward (or even the best) alternative to predict the physicochemical properties of ILs.

This review covers a diverse set of GCMs that have been reported and applied to predict thermodynamic properties of ILs that are relevant for the design, simulation, optimization and control of separation systems and reaction units. A detailed description of these GCMs is provided thus highlighting their application in the calculation of different ILs thermodynamic properties. This manuscript provides to interested readers an easy and comprehensive survey of GCMs for identifying and selecting the best alternatives to estimate several physicochemical properties of ILs.

2. Group contribution models for the calculation of thermodynamic properties of ionic liquids

2.1. Basis and fundamentals of group contribution models

In GCMs, the thermodynamic property estimation is carried out considering the contributions and frequencies of the elements (e.g., atoms, functional groups, ions) that conform the IL molecular structure (Valderrama et al., 2012; Gani, 2019). They assume that the contribution of each element for the thermodynamic property calculation should be the same in any molecule independently of its structure (Nannoolal et al., 2007). Fig. S3 illustrates the concept of GCMs for the prediction of a given thermodynamic property using an IL molecule as example. The molecular element contributions of the model are calculated from an experimental database of the desired thermodynamic property that contains similar compounds from the target chemical family.

The development and implementation of GCMs consists of three stages: a) the definition of elements (i.e., atoms, functional groups, ions) to obtain the molecular structure of target compounds or chemical family, b) the determination of equation(s) and functionalities to calculate and estimate the thermodynamic property based on the type of structural elements and their frequencies including other additional molecular parameters if any and c) the stage of numerical calculation of structural element contribution values for the thermodynamic property at hand, which usually implies a nonlinear regression process using an experimental database (Su et al., 2017). In the first stage, the target compounds are divided into their structural elements considering their

molecular complexity and available experimental information. Then, an equation or model (explicit or implicit) is defined to establish the functionality of the thermodynamic property to be calculated with respect to these structural elements and their frequencies. This equation/functionality can also include other parameters or characteristics available for the compound under analysis (e.g., molecular weight, number of atoms, bond types) and also state variables (e.g., temperature, pressure). Finally, the values of structural element contributions to be used in the equation/functionality are determined by data regression techniques using experimental values of the target thermodynamic property. This last stage implies the resolution of a parameter identification problem where a proper objective function should be minimized via the implementation of a local or global optimization method.

GCMs can be classified into additive, additive-correlative, interaction-based and high order models (Ghasemitarbar and Movagharnajad, 2016). Additive GCMs assume that the property depends on the number of structural elements, while the additive-correlative GCMs introduce additional known molecular properties into the model. Interaction-based GCMs calculate the property using additional parameters that describe the interactions between the structural elements that conform the molecule. Higher-order GCMs introduce variables to describe the spatial distribution of structural elements of tested molecules and can also contain first-order groups.

Different GCMs have been reported and applied to calculate the physicochemical properties of ILs and a summary of their applications is given in Tables 1–11. A detailed description of different GCMs for the estimation of relevant thermodynamic properties of ILs is provided in the next subsections thus discussing its main characteristics, application range and results obtained from their implementation. Two statistical metrics have been considered in the discussion of GCMs performance: the average absolute relative deviation (AARD, %) and absolute relative deviation (ARD, %), which are given by

$$AARD = \frac{100 \cdot \sum_{i=1}^{N_{dat}} |(X^{cal} - X^{exp})/X^{exp}|_i}{N_{dat}} \quad (1)$$

$$ARD_i = 100 \cdot |(X^{cal} - X^{exp})/X^{exp}|_i \quad (2)$$

where X^{cal} is the calculated property value, X^{exp} is the experimental property value and N_{dat} is the number of experimental data analyzed in the corresponding study.

2.2. Heat capacity

Heat capacity is a basic input data in process simulation software for energy transfer and thermodynamic calculations like entropy and enthalpy changes of reactive and non-reactive systems (Valderrama et al., 2011c; Chen et al., 2019). It is defined as the dependence of enthalpy with respect to the temperature of a given compound (Gardas and Coutinho, 2008a). This property is essential for the design and scale up of distillation, evaporation, extraction and heating systems (Valderrama et al., 2011c; Nancarrow et al., 2015). The variation in heat capacity allows to understand the changes in the compound structure and also provides information on phase changes (Gardas and Coutinho, 2008a). The experimental information of ILs heat capacities is relatively scarce considering the vast amount of these compounds where the

Table 1 – GCMs performance for the heat capacity prediction of ILs.

Model	Modeling performance ¹				
	N _{IL}	N _{dat}	AARD, %	R ²	Remarks
GCM					
Gardas and Coutinho (2008a)	19	2396	0.36	0.99	Global set
Soriano et al. (2010a)	32	3149	0.69	N/A	Global set
Valderrama et al. (2011c)	32	469	2.80	N/A	Correlation set
	9	65	2.60	N/A	Prediction set
Müller and Albert (2014)	84	2234	1.40	N/A	Correlation set
	20	209	4.40	N/A	Prediction set
Albert and Müller (2014)	86	2210	2.58	0.98	Correlation set
	20	209	5.44	0.94	Prediction set
Ahmadi et al. (2015)	100	4072	5.83	N/A	Correlation set
	28	750	5.61	N/A	Prediction set
Nancarrow et al. (2015)	92	2485	6.76	N/A	Lego approach
	45	1586	5.54	N/A	Lego approach
	45	1586	5.30	N/A	Meccano approach
Chen et al. (2019)	44	2391	0.39	N/A	Correlation set
	17	913	0.62	N/A	Prediction set
GCM-CSP	53	961	2.91	N/A	Global set
Ge et al. (2008)					
GCM-GFA	82	3726	1.68	0.99	Global set
Sattari et al. (2014a)	65	2939	1.68	0.99	Correlation set
	17	787	1.65	0.99	Prediction set
AI (GMDH)	56	2940	1.84	0.98	Global set
Rostami et al. (2019)					

¹ Variable description:
N_{IL}: Number of ILs used in the study.
N_{dat}: Number of experimental data analyzed in the study.
R²: Coefficient of determination.
N/A: Data not available.

available data have been reported for specific ILs (Gardas and Coutinho, 2008a). Different GCMs for calculating the heat capacity of ILs are summarized in Table 1.

Gardas and Coutinho (2008a) developed a second-order GCM to estimate the liquid heat capacity (C_{pL} , J/molK) of ILs based on pyrrolidinium, pyridinium and imidazolium cations and trifluoromethane sulfonate, ethyl sulfate, bromide, bis (trifluoromethanesulfonyl) amide, tetrafluoroborate and hexafluorophosphate anions. This GCM was formulated employing the approach proposed by Růžička and Domalski (1993a) (1993b) for the estimation of pure organic liquids heat capacities as a function of temperature. This model is described by the following equations

$$C_{pL} = R \left[A_1 + A_2 \left(\frac{T}{100} \right) + A_3 \left(\frac{T}{100} \right)^2 \right] \quad (3)$$

$$A_1 = \sum_{i=1}^k n_i a_{1i} \quad (4)$$

$$A_2 = \sum_{i=1}^k n_i a_{2i} \quad (5)$$

$$A_3 = \sum_{i=1}^k n_i a_{3i} \quad (6)$$

where T is the temperature (K), n_i is the frequency of the structural element i contained in the ILs molecule, k is the total number of different structural elements, a_{1i} , a_{2i} and a_{3i} are the structural element contributions to the model parameters A_i and $R = 8.314472$ J/mol K is the universal gas constant. This model is capable to predict ILs heat capacities from 264.8 to 825 J/mol K at 196.36–663.10 K with AARD = 0.36 %, see Table 1. However, this model was limited to estimate

the property for a few ILs families where a total of 2396 experimental data points from 19 ILs including 6 anions and 3 cations were used to develop this GCM. To overcome this drawback, Chen et al. (2019) extended this model to more families of ILs where 3304 data points at 189.66–524.87 K from 61 ILs (based on 6 cations and 14 anions) were utilized. The modeling errors obtained with this GCM were similar to those obtained with the Gardas and Coutinho (2008a) model (i.e., AARD < 5 %).

GCM proposed by Joback (1984) for the prediction of ideal gas heat capacities was modified to estimate ILs heat capacities using a corresponding states principle (CSP) (Ge et al., 2008). The authors included 3 additional groups (B, P and -SO₂-) commonly found in ILs. The database utilized to develop this model consisted of 961 heat capacity data points from 53 ILs (e.g., [C_nmim][OTf], [C₄mim][BF₄], [C₄mim][PF₆], [C₄mpyrr][FAP]). The ideal gas heat capacities (C_{pig} , J/mol K) of ILs as a function of temperature were calculated by

$$C_{pig} = \left[\sum_i n_i B_{1Cpi} - 37.93 \right] + \left[\sum_i n_i B_{2Cpi} + 0.210 \right] T + \left[\sum_i n_i B_{3Cpi} - 3.91 \cdot 10^{-4} \right] T^2 + \left[\sum_i n_i B_{4Cpi} + 2.06 \cdot 10^{-7} \right] T^3 \quad (7)$$

where B_{iCpi} is the corresponding structural element contribution. The liquid heat capacities C_{pL} were estimated using CSP (Poling et al., 2001) as a function of C_{pig} and other thermodynamic properties of ILs as follows

$$\frac{C_{pL} - C_{pig}}{R} = 1.586 + \frac{0.49}{1 - T_r} + \omega \left[4.2775 + \frac{6.3(1 - T_r)^{1/3}}{T_r} + \frac{0.4355}{1 - T_r} \right] \quad (8)$$

Table 2 – GCMs performance for the density prediction of ILs.

Model	Modeling performance ¹				Remarks
	N _{IL}	N _{dat}	AARD, %	R ²	
GCM					
Gardas and Coutinho (2008c)	12	1086	0.45	N/A	Imidazolium-based ILs.
	8	435	1.43	N/A	Pyridinium-, pyrrolidinium- and phosphonium-based ILs.
Lazzús (2010a)	310	310	1.93	0.97	Global set (V ₀ and ρ ₀ estimation)
	210	210	1.90	0.97	Correlation set (V ₀ and ρ ₀ estimation)
	100	100	1.98	0.95	Prediction set (V ₀ and ρ ₀ estimation)
	76	3530	0.73	0.99	Density as a function of T and P estimation
Qiao et al. (2010)	120	6562	0.88	N/A	Correlation set
	3	188	0.27	N/A	Prediction set
Aguirre and Cisternas (2012)	20	108	1.57	N/A	Ammonium-based ILs
Paduszyński and Domańska (2012)	1028	16,830	0.51	N/A	Global set
	828	13,135	0.53	N/A	Correlation set
	200	3695	0.45	N/A	Prediction set
Evangelista et al. (2014)	864	21,845	0.83	N/A	Global set
Taherifard and Raeissi (2016)	N/A	25,850	0.95	N/A	Global set
	N/A	12,516	1.02	N/A	Correlation set
	N/A	13,334	0.89	N/A	Prediction set
Chen et al. (2019)	143	7360	0.49	N/A	Global set
	90	5039	0.43	N/A	Correlation set
	53	2321	0.67	N/A	Prediction set

¹ Variable description:
N_{IL}: Number of ILs used in the study.
N_{dat}: Number of experimental data analyzed in the study.
R²: Coefficient of determination.
N/A: Data not available.

$$T_r = \frac{T}{T_c} \quad (9)$$

where ω is the acentric factor, T_r is the reduced temperature and T_c is the ILs critical temperature. The main drawback of this model is that the values of normal boiling point (T_b) and critical properties (T_c, P_c, V_c) of ILs are needed and, consequently, its application could be restricted due to the lack of experimental information on these properties for several ILs. Therefore, these authors proposed to estimate the missing thermodynamic properties via the GCM proposed by

Valderrama and Robles (2007), see Sections 2.11 and 2.12 of this review.

Soriano et al. (2010a) proposed a GCM approach using 3149 heat capacity data from 32 ILs. C_{pL} of ILs was estimated by adding the cation and anion contributions as follows

$$C_{pL} = C_{p, \text{ cation}} + C_{p, \text{ anion}} \quad (10)$$

$$C_{p, \text{ ion}} = C_1 + C_2 \cdot \left(\frac{T}{K}\right) + C_3 \cdot \left(\frac{T}{K}\right)^2 \quad (11)$$

Table 3 – GCMs performance for the viscosity prediction of ILs.

Model	Modeling performance ^a				Remarks
	N _{IL}	N _{dat}	AARD, %	R ²	
GCM					
Gardas and Coutinho, (2008b)	29	498	7.78	0.99	Global set
Gardas and Coutinho (2009)	25	482	7.50	0.99	Global set
Gharagheizi et al. (2012a)	443	1672	6.32	0.87	Global set
Daniel et al. (2013)	4	20	7.64	0.98	Global set
Lazzús and Pulgar-Villarroel, (2015)	326	1445	4.55	0.94	Global set
	183	1110	4.46	N/A	Correlation set
	143	335	4.84	N/A	Prediction set
Sattari et al. (2016a)	85	863	3.23	0.98	Global set
	N/A	667	2.91	0.98	Correlation set
	N/A	196	4.31	0.97	Prediction set
Chen et al., (2019)	76	1090	3.58	N/A	Global set
	56	778	3.36	N/A	Correlation set
	20	312	5.63	N/A	Prediction set

N_{IL}: Number of ILs used in the study.
N_{dat}: Number of experimental data analyzed in the study.
R²: Coefficient of determination.
N/A: Data not available.
^a Variable description:

Table 4 – GCMs performance for the thermal conductivity prediction of ILs.

Model	Modeling performance ^a				Remarks
	N _{IL}	N _{dat}	AARD, %	R ²	
GCM					
Gardas and Coutinho (2009)	16	107	1.06	0.99	Global set
Gardas et al. (2010)	11	75	0.67	0.94	Global set
Wu et al. (2013)	36	286	1.66	N/A	Global set
Albert and Müller, (2014)	32	316	2.49	0.95	Correlation set
	7	59	8.09	0.74	Prediction set
Lazzús (2015)	41	400	2.12	0.98	Global set
	30	300	1.90	0.99	Correlation set
	11	100	2.33	0.97	Prediction set
Soares et al. (2019)	33	237	1.16	N/A	Global set

N_{IL}: Number of ILs used in the study.

N_{dat}: Number of experimental data analyzed in the study.

R²: Coefficient of determination.

N/A: Data not available.

^a Variable description:

Table 5 – GCMs performance for the melting point prediction of ILs.

Model	Modeling performance ¹			Remarks
	N _{IL}	AARD, %	R ²	
GCM				
Huo et al. (2009)	190	5.86	0.90	Global set
Lazzús (2012b)	400	7.07	0.88	Global set
	200	7.97	N/A	Correlation set
	200	6.16	N/A	Prediction set
Aguirre et al. (2012)	136	7.80	N/A	Global
Gharagheizi et al. (2012c)	799	5.82	0.81	Global set
	598	5.81	0.81	Correlation set
	201	5.85	0.82	Prediction set
Chen et al. (2019)	111	4.70	N/A	Global set
	75	4.70	N/A	Correlation set
	26	7.09	N/A	Prediction set
Valderrama and Cardona (2021)	124	6.47	N/A	Correlation set
	13	6.93	N/A	Prediction set

¹ Variable description:
N_{IL}: Number of ILs used in the study.
R²: Coefficient of determination.
N/A: Data not available.

Table 6 – GCMs performance for the surface tension prediction of ILs.

Model	Modeling performance ^a				Remarks
	N _{IL}	N _{dat}	AARD, %	R ²	
GCM					
Gharagheizi et al. (2012b)	51	920	3.61	0.92	Global set
	50	735	3.71	0.92	Correlation set
	45	185	3.20	0.93	Prediction set
Lazzús et al. (2017b)	154	2286	2.81	0.98	Global set
	118	1804	2.69	0.99	Correlation set
	36	482	3.36	0.98	Prediction set
Shahsavari et al. (2018)	61	1246	4.16	0.92	Global set
	N/A	872	4.19	0.92	Correlation set
	N/A	374	4.11	0.91	Prediction set
Chen et al. (2019)	102	1365	3.10	N/A	Global set
	72	952	2.87	N/A	Correlation set
	30	413	4.71	N/A	Prediction set
GCM-CSP					
Wu et al. (2012)	105	1224	4.95	N/A	Global set

N_{IL}: Number of ILs used in the study.
N_{dat}: Number of experimental data analyzed in the study.
R²: Coefficient of determination.
N/A: Data not available.
^a Variable description:

where $C_{p,ion} = C_{p,cation}$ or $C_{p,anion}$ are the contributions to the molar heat capacity of cation and anion that conformed the tested IL and C_i is an adjustable empirical parameter specific for each ion. The major limitation of this model relies on its applicability to a reduced number of IL molecules that can be obtained from 10 cations and 14 anions that were defined for the database of structural element contributions. Müller and Albert (2014) proposed a similar GCM to calculate the heat capacity of more ILs. This property can be estimated for 1248 pure ILs using this model via the contributions from 39 cations and 32 anions. 2443 heat capacity experimental data from 104 ILs were used to develop this GCM. The modeling errors obtained in the correlation stage were acceptable with AARD = 1.4 %. The modeling errors increased to predict heat capacities of ILs not used in the data correlation stage (i.e., AARD = 4.4 %), see Table 1. The model of these authors was based on the cation and anion contributions (Albert and Müller, 2014), which was defined as

$$C_{pL} = (D_{1cation} + D_{1anion}) - (D_{2cation} + D_{2anion}) \cdot T + (D_{3cation} + D_{3anion}) \cdot T^2 \quad (12)$$

$$D_{1ion} = \sum_i (\nu_i \cdot D_{1i}) + D_{1correction} \quad (13)$$

$$D_{2ion} = \sum_i (\nu_i \cdot D_{2i}) + D_{2correction} \quad (14)$$

$$D_{3ion} = \sum_i (\nu_i \cdot D_{3i}) + D_{3correction} \quad (15)$$

where ν_i is the frequency of structural element i contained in the ion, D_{1i} , D_{2i} and D_{3i} are the structural element contributions and $D_{icorrection}$ corresponds to additional contributions related to the ion type or ring structure. The heat capacity database included 2419 experimental data from 106 ILs covering a temperature range of 190–663.1 K.

Another GCM for predicting the heat capacities of ILs containing alkyl-ammonium, phosphonium, pyrrolidinium, pyridinium and imidazolium was reported by Valderrama

Table 7 – GCMs performance for the electrical conductivity prediction of ILs.

Model	Modeling performance ¹				Remarks
	N _{IL}	N _{dat}	AARD, %	R ²	
GCM					
Gardas and Coutinho (2009)	15	307	4.57	0.99	Global set
Wu et al. (2016)	188	2195	6.02	N/A	Global set
	177	1978	6.12	N/A	Correlation
	11	217	5.10	N/A	Prediction
Chen et al. (2020)	77	1578	3.62	N/A	Global set
	57	1121	3.30	N/A	Correlation set
	20	457	6.83	N/A	Prediction set
GCM-LSSVM					
Gharagheizi et al. (2014)	54	1077	3.30	0.99	Global set

¹ Variable description:
N_{IL}: Number of ILs used in the study.
N_{dat}: Number of experimental data analyzed in the study.
R²: Coefficient of determination.
N/A: Data not available.

Table 8 – GCMs performance for the refractive index prediction of ILs.

Model	Modeling performance ¹				Remarks
	N _{IL}	N _{dat}	AARD, %	R ²	
GCM					
Gardas and Coutinho (2009)	24	245	0.18	0.99	Global set
Sattari et al. (2014b)	97	931	0.34	0.96	Global set
	82	759	0.32	0.97	Correlation set
	15	172	0.45	0.92	Prediction set
Wang et al. (2017)	299	2138	0.63	0.89	Global set
	277	1711	0.63	0.88	Correlation set
	190	427	0.60	0.90	Prediction set

¹ Variable description:
N_{IL}: Number of ILs used in the study.
N_{dat}: Number of experimental data analyzed in the study.
R²: Coefficient of determination.

Table 9 – GCMs performance for the thermal decomposition temperature prediction of ILs.

Model	Modeling performance ¹			Remarks
	N _{IL}	AARD, %	R ²	
GCM				
Lazzús (2012c)	198	4.28	0.94	Global set
	120	4.34	N/A	Correlation set
	78	4.18	N/A	Prediction set
Gharagheizi et al. (2013)	613	4.40	0.85	Global set
	489	4.50	0.85	Correlation set
	124	4.30	0.86	Prediction set
Mokadem et al. (2016)	639	4.22	0.87	Global set
	499	4.28	0.86	Correlation set
	140	4.02	0.90	Prediction set

¹ Variable description:
N_{IL}: Number of ILs used in the study.
R²: Coefficient of determination.
N/A: Data not available.

Table 10 – GCMs performance for the critical properties and normal boiling point prediction of ILs.

Model	Modeling performance ¹			Remarks
	N _{IL}	AARD, %	Remarks	
GCM				
Valderrama and Robles (2007)	50	5.20		Density test.
Valderrama et al. (2008)	200	5.90		Density test.
Valderrama et al. (2012)	526	15		Density test.
	1130	7		Vapor pressure test.
	667	4.76		Density test.
Valderrama et al. (2015)	1630	2.80		Vapor pressure test.
	637	6.20		Density test.
Valderrama et al. (2021)	4295	3.10		Vapor pressure test.
	747	4.40		
GC-PT Shen et al. (2011)				
FC-CS Huang et al. (2013)	490	3.30		

¹ Variable description:
N_{IL}: Number of ILs used in the study.

et al. (2011c). This model included an additional structural parameter known as mass connectivity index (φ), which was studied by Valderrama and Rojas (2010). This parameter considers the type of connections between groups and their molecular mass

$$\varphi = \sum \left(\frac{1}{\sqrt{m_i m_j}} \right)_{ij} \quad (16)$$

where m_i and m_j are the mass of neighboring groups i and j in a given IL molecule. The functionality of ILs heat capacity with temperature was described as

$$C_{pL} = C_{p0} - 100.70\varphi + \varphi(0.3918T - 1.952 \cdot 10^{-4}T^2) \quad (17)$$

$$C_{p0} = 9.0045 + n_i E_{0i} \quad (18)$$

where C_{p0} (J/mol K) is the heat capacity reference value determined by GCM using data of C_{pL} at 298 K only for ILs that are truly liquids at this operating condition, E_{0i} is the contribution value of structural element i and T_0 is the reference T (i.e., 298.15 K). This GCM was formulated via the processing and analysis of 534 heat capacity data (368–1368 J/mol K) at 250 – 426 K from 41 ILs. 126 compounds were employed for the correlation stage of this model. It was reported AARD < 3 % for the ILs heat capacity estimation with this approach. However, its main limitation relies on the knowledge of a reference heat capacity value, which is sometimes not available especially for new ILs.

Ahmadi et al. (2015) proposed an atomic-based GCM that can be applied in a wide range of temperatures (190–663.10 K) and heat capacities (93 – 1764, J/mol K). This model is given by the next equation

$$C_{pL} = 0.2802T^{1.0854} - 17.5066\ln(T) + 0.6593W^{1.0793} + 15.9932Nu_{Ca} + 16.1292Nu_{Cc} - 2.8956Nu_N - 11.7667Nu_S - 1.3729Nu_O - 4.1977(Nu_F + Nu_{Br} + Nu_{Cl}) + 6.7438Nu_B - 12.3990 \quad (19)$$

where Nu_{Ca} , Nu_{Cc} , Nu_N , Nu_S , Nu_O , Nu_F , Nu_{Br} , Nu_{Cl} and Nu_B are the number of carbon atoms in anion, the carbon atoms in cation, the number of atoms of nitrogen, sulfur, oxygen, fluorine, bromine, chlorine and boron in the IL, respectively. These authors used 4822 heat capacity data points from 128

Table 11 – GCMs performance for the prediction of other thermodynamic properties of ILs.

Model	Property	Modeling performance ¹				Remarks
		N _{IL}	N _{dat}	AARD, %	R ²	
GCM						
Lazzús (2016a)	Freezing point	63	63	5.30	0.94	Global set
		40	40	5.34	0.95	Correlation set
		23	23	5.25	0.91	Prediction set
Gardas and Coutinho (2009)	Isobaric expansivity	49	109	1.98	0.99	Global set
Gardas and Coutinho (2009)	Isothermal compressibility	22	26	2.53	0.99	Global set
Zhou et al. (2014)	Static dielectric constant	58	128	7.41	N/A	Global set

¹ Variable description:
N_{IL}: Number of ILs used in the study.
N_{dat}: Number of experimental data analyzed in the study.
R²: Coefficient of determination.
N/A: Data not available.

ILs to develop this GCM. Results showed that this model was outperformed by the model of Müller and Albert (2014). However, the advantage of this GCM relies on its wide application for different ILs since the molecules are represented only as atomic-level contributions.

Nancarrow et al. (2015) implemented and compared the accuracy of two GCMs based on Meccano and Lego approaches. This classification relies on size and nature of the structural building blocks or structural elements employed in each model. Meccano approach uses large functional groups such as ions, e.g.: the model of Gardas and Coutinho (2008a). This type of models is generally more accurate, see Table 1, but its application range is limited. On the other hand, the Lego approach is based on the use of simple and small structural elements. The model reported by Ge et al. (2008) falls in this category and is an illustrative example of this approach. These models are less accurate than those based on the Meccano approach. However, they can be applied to construct more IL molecules in comparison to the Meccano-based GCMs. For illustrative purposes, Fig. S4 exemplifies the structural elements considered in the Meccano and Lego approaches. These authors used a refined database containing 2642 experimental data from 96 ILs to evaluate GCMs based on both approaches. This database was divided into two sub-databases: one containing 2584 data from 92 ILs to implement the Lego approach and another sub-database constituted by 1586 data from 45 ILs that were used with both Meccano and Lego approaches. As expected, the Meccano-based GCM outperformed the predictions obtained with the Lego-based GCM, see results given in Table 1.

Other thermodynamic models based on the combination of GCMs with other numerical tools have been reported to estimate C_{pL} of ILs. For instance, Sattari et al. (2014a) used a GCM combined with genetic function approximation (GFA) to estimate C_{pL} of imidazolium-, phosphonium-, pyridinium-, pyrrolidinium- and ammonium-based ILs consisting of 39 cations and 24 anions at atmospheric pressure. The database employed for the model development consisted of 3726 heat capacity experimental data from 82 ILs covering 180.06–663 K and heat capacity values from 259.09 to 1805.7 J/mol K. GFA is a feature selection method proposed by Rogers and Hopfinger (1994) that allowed to choose the most effective functional groups for the prediction of this thermodynamic property. A hybrid group method of data handling (GMDH), which can be considered as a version of neural network-based system, was proposed to estimate the heat capacity of

ILs at 188.06–663.10 K (Rostami et al., 2019). 2940 heat capacity data (226–1413 J/mol K) from 56 ILs were used to develop this model. The input parameters were T, the number of methyl groups in the IL cation, the number of hydrogen atoms in the anions and the number of atoms in both IL cation and anion. It showed AARD = 1.84 % to predict the ILs heat capacities.

2.3. Density

Density is a relevant property of ILs that is required to estimate process equipment sizes, to solve material/energy balance equations and to correlate other thermophysical properties like surface tension and viscosity (Gardas and Coutinho, 2008c; Mendonça et al., 2012; Padaszyński and Domańska, 2012). It has been estimated that the experimental values of density for more than 1000 ILs is available in databases, which have been used to develop models for its estimation including GCMs (Padaszyński and Domańska, 2012; Keshavarz et al., 2016b).

Ye and Shreeve (2007) developed a simple GCM to calculate the densities (ρ , g/cm³) at room-temperature of ILs containing imidazolium, triazolium, tetrazolium and tetraalkylammonium cations and tetrafluoroborate, hexafluorophosphate, bis(trifluoromethanesulfonyl) amide, nitrate, perchlorate and dinitramide anions. This model is given by the next expression

$$\rho = \frac{W}{NV} \quad (20)$$

where W is the ILs molar mass (g/mol), N is the Avogadro constant and V is the IL molar volume (cm³/mol). V was assumed to be a linear function of the volumes of cation (V_+) and anion (V_-) as described by Jenkins et al. (1999) (i.e., for a specific CA_pANI_q IL, $V = pV_+ + qV_-$). This GCM was limited to estimate the densities of ILs at atmospheric pressure and 298.15 K. To overcome this disadvantage, Gardas and Coutinho (2008c) modified this model to expand its application range at 273.15 – 393.15 K and 0.10 – 100 MPa. They assumed that the mechanical coefficients (i.e., isobaric expansivity and isothermal compressibility) of the ILs involved in their study were similar and also constant over a wide range of temperature and pressure. Therefore, they proposed the next expression to calculate ρ (kg/m³) as a function of temperature (T , K) and pressure (P , MPa)

$$\rho = \frac{W}{NV_0(8.005 \cdot 10^{-1} \pm 2.333 \cdot 10^{-4} + 6.652 \cdot 10^{-4} \pm 6.907 \cdot 10^{-7} K^{-1} T - 5.919 \cdot 10^{-4} \pm 2.410 \cdot 10^{-6} MPa^{-1} P)} \quad (21)$$

where V_0 is the molar volume (m^3/mol) at the reference temperature (T_0 , K) and reference pressure (P_0 , MPa) and W is given in kg/mol . 1086 experimental data from 12 imidazolium-based ILs and 435 experimental data from 8 phosphonium-, pyridinium- and pyrrolidinium-based ILs were used to develop this GCM. It showed AARD values from 0.45 % to 1.57 % for the density calculation of pyrrolidinium-, pyridinium-, phosphonium- and imidazolium-based ILs, see Table 2. Aguirre and Cisternas (2012) extended this model for the ρ estimation of ammonium-based ILs. 108 experimental data from 20 ammonium-based ILs were used for the correlation of Equation [21]. AARD of this model ranged from 0.07 % to 5.09 % for these ILs.

A simple GCM to predict V_0 ($m^3/kmol$) and a linear relation to calculate ρ of ILs at 258–393 K and 0.09–207 MPa were proposed by Lazzús (2010a), which are defined as

$$V_0 = 0.042 + \sum_i n_i \Delta V_{c_i} + \sum_j n_j \Delta V_{a_j} \quad (22)$$

$$\rho_0 = W \cdot V_0^{-1} \quad (23)$$

$$\rho = \rho_0 - 0.7190(T - T_0) + 0.5698(P - P_0) \quad (24)$$

where ρ_0 (kg/m^3) is the density at $T_0 = 298.15$ K and $P_0 = 0.101$ MPa, W is given in $kg/kmol$, ΔV_c and ΔV_a are the structural element contributions for the cation and the anion to the molar volume, respectively. This GCM was formulated with an experimental database that included the molar volume of 310 ILs at 298.15 K and 0.101 MPa. 92 ion groups were defined: 26 cation groups (e.g., pyrazolium, sulfonium, ammonium, phosphonium, guanidinium, oxazolidinium, morpholinium, piperidinium, pyrrolidinium, pyridinium and imidazolium) and 66 anion groups (e.g., metal complexes, trifluoroacetates, triflates, carboxylates, phosphates, borates, amides, imides, tosylates, sulfonates, sulfates, pseudohalides and halides). ρ was calculated as a linear function of T and P via Equation [24] where the model parameters were determined with 3530 experimental data (869 – 1641 kg/m^3) of 76 ILs at 258 – 393 K and 0.09 – 207 MPa. It showed AARD = 0.73 % with $ARD < 8$ % for the estimation of density of tested ILs.

Qiao et al. (2010) proposed another GCM to predict ρ (g/cm^3) of ILs using T and P as follows

$$\rho = H_1 + H_2 P + H_3 T \quad (25)$$

$$H_1 = \sum_{i=1}^{51} n_i h_{1i} + 0.781297 \quad (26)$$

$$H_2 = \sum_{i=1}^{51} n_i h_{2i} + 0.0000976606 \quad (27)$$

$$H_3 = \sum_{i=1}^{51} n_i h_{3i} - 0.000742764 \quad (28)$$

where h_{1i} , h_{2i} and h_{3i} are the contributions of the structural element i for H_1 , H_2 and H_3 , respectively. 6750 experimental density data from 123 pure ILs including quaternary phosphonium, imidazolium, pyridinium, pyrrolidinium and piperidinium besides compounds of MCl_x family were utilized to develop this model where 51 functional groups were defined.

It showed AARD values of 0.88 % and 0.27 % in the data correlation and prediction tests.

Paduszyński and Domańska (2012) reported a GCM based on an extensive experimental density database with 6830 values at 253 – 473 K and 0.1 – 300 MPa from 1028 ILs including amino acid and dicationic and tricationic compounds. Therefore, 177 groups were defined for this GCM. These authors estimated V_0 (m^3/mol) at T_0 and P_0 using the next expression

$$V_0 = \sum_i n_i v_i^0 \quad (29)$$

where v_i^0 is the contribution of the structural element i . ρ_0 of ILs at T_0 and P_0 was then calculated using Equation [23]. Then, the density ρ (T, P_0) in kg/m^3 at P_0 can be calculated via the next equation

$$\rho(T, P_0) = \frac{W}{V_0 [1 + 6.439 \cdot 10^{-4} K^{-1} (T - T_0)]} = \frac{\rho_0}{1 + 6.439 \cdot 10^{-4} K^{-1} (T - T_0)} \quad (30)$$

Tait-type equations were proposed for the calculation of ρ (kg/m^3) of compressed ILs

$$\rho = \frac{\rho(T, P_0)}{1 - 0.081 \ln[1 + (P - P_0)J(T)]} \quad (31)$$

$$J(T) = \frac{1}{195 MPa} [1 + 4.97 \cdot 10^{-3} K^{-1} (T - T_0)] \quad (32)$$

This model accurately predicted the densities of a wide diversity of ILs where AARD = 0.45 % for 3695 experimental data from 200 ILs, see Table 2.

Evangelista et al. (2014) reported an extension of GCM proposed by Elbro et al. (1991) for the calculation of saturated liquid densities of ILs. This modified model was developed using a database with 21,845 experimental density values from 864 ILs including dicationic and tricationic species at 251.62–473.15 K and 0.1–300.0 MPa. These authors incorporated 102 new IL groups to those reported by Ihmel and Gmehling (2003). The cation groups were classified into “first level cation groups” (i.e., groups directly attached to atoms of the rings) and “second level groups” (i.e., groups directly attached to the “first level cation groups”), while the anion groups were obtained with the same methodology but the largest anions were divided into smaller groups considering the “first level anion groups”. This approach allowed to reduce the number of groups to obtain a wide variety of anions and cations involved in the database. Then, the saturated liquid densities (ρ_{sat} , g/cm^3) were estimated using the next equation

$$\rho_{sat} = \frac{W}{V} = \frac{W}{\sum n_i \Delta v_i} \quad (33)$$

$$\Delta v_i = L_{1i} + L_{2i} T + L_{3i} T^2 \quad (34)$$

where L_{1i} (cm^3/mol), L_{2i} ($cm^3/mol K$) and L_{3i} ($cm^3/mol K^2$) are the model parameters. The next Tait-type equation was employed to predict ρ (g/cm^3)

$$\rho = \frac{\rho(T, P_0)}{1 - 0.0711 \ln \left[\frac{(M_2 + P)}{M_2 + P_0} \right]} \quad (35)$$

$$M_2 = 287.624 MPa - 0.444 \frac{MPa}{K} T \quad (36)$$

where ρ (T, P_0) is also given in g/cm^3 . AARD values of this model were 0.676 % for imidazolium-, 1.21 % for

ammonium-, 1.28 % for pyridinium-, 0.81 % for pyrrolidinium-, 0.80 % for phosphonium-, 2.15 % for piperidinium-, 1.51 % for morpholinium-, 1.93 % for azepanium-, 0.45 % for pyrazolium-, 0.42 % for isoquinolinium- and 0.24 % for quinolinium-based ILs.

Taherifard and Raeissi (2016) pointed out that several GCMs to predict ILs densities are based in large functional groups (i.e., cations, anions), which could improve the model accuracy but limits its applicability for different ILs. These authors proposed a simple GCM using only atoms and small functional groups to cover different ILs using the next equations

$$\rho = \frac{W}{V} \quad (37)$$

$$V = d_m + \frac{N_{at}}{100} (-20.8279 + 0.3749T - 0.2489P) \quad (38)$$

$$d_m = -4.0059 - 17.3357n_r + \sum n_i V_{c_{i1}} + \sum n_j V_{a_{1j}} \quad (39)$$

where n_r is the total number of rings existing in the IL, V_{c_i} and V_{a_j} are the contributions of the functional groups for the cation and anion, respectively and N_{at} is the number of atoms in the IL structure. These authors applied an experimental database containing 25,850 density values at 217.58–473.15 K and 0.1–300 MPa. Results showed that AARD of this approach was similar to that obtained with other GCMs based on large functional groups for cations and anions. This model was also compared with the models reported by Gardas and Coutinho (2008c) and Paduszyński and Domańska (2012). The performance of the model of Paduszyński and Domańska (2012) (i.e., AARD = 0.57 %) was better than that obtained with this new approach (i.e., AARD = 0.76 %). However, the model proposed by Gardas and Coutinho (2008c) (i.e., AARD = 1.3 %) was outperformed by the model proposed by Taherifard and Raeissi (2016) (i.e., AARD = 0.58 %).

Chen et al. (2019) developed a GCM using a database with 7360 experimental values of 143 ILs including 18 anions, 6 cations and 3 side groups thus covering temperatures of 273.15–473.15 K and pressures of 0.1–250.7 MPa. This model is given by

$$\rho = Q_1 + Q_2T + Q_3P \quad (40)$$

$$Q_1 = \sum_{i=1}^k n_i q_{1i} \quad (41)$$

$$Q_2 = \sum_{i=1}^k n_i q_{2i} \quad (42)$$

$$Q_3 = \sum_{i=1}^k n_i q_{3i} \quad (43)$$

where ρ is reported in kg/m^3 , q_{1i} , q_{2i} and q_{3i} are the structural element contributions. AARD values of this model were 0.43 % and 0.67 % for the correlation and prediction tests, respectively. In order to improve the reliability of the model parameters, these authors tried another correlation test using all ILs experimental data for the correlation set with the aim of enhancing the GCM performance. AARD = 0.49 % for this improved model with a maximum ARD value of 4.60 %.

2.4. Viscosity

Viscosity is the thermodynamic property utilized to measure the internal resistance of a fluid to flow and it is related to the internal friction within the fluid caused by the intermolecular interactions (Gardas and Coutinho, 2008b; Rooney et al., 2010). The design, simulation and optimization of reactors, crystallization equipment, distillation columns, liquid-liquid extractors, heat transfer equipment, stripping columns and process piping rely on this property for both pure compounds and mixtures (Lazzús and Pulgar-Villarroel, 2015; Chen et al., 2019; Hosseini et al., 2019). ILs are characterized by a high viscosity that could limit their application in industrial processes involving operations like pumping, mixing, heat and mass transfer (Aparicio et al., 2010; Chen et al., 2019; Sattari et al., 2016a). For comparison, the room temperature viscosities of ILs can range from 10 up to more than 10^5 cP, while the organic solvents have viscosities from 0.2 to 10 cP (Gardas and Coutinho, 2008b). The application of ILs as solvents requires a low viscosity to minimize the pumping costs and to increase the mass transfer rates (Gardas and Coutinho, 2008b). On the other hand, the high viscosities of ILs favor their utilization as lubricants (Lazzús and Pulgar-Villarroel, 2015). This property is highly dependent on the type of anion and cation that conforms the ILs molecule (Rooney et al., 2010). This context opens the possibility of preparing ILs with a tailored viscosity for the desired application (Aparicio et al., 2010). However, different authors (e.g., Aparicio et al., 2010; Chen et al., 2019) have highlighted that the experimental viscosity data of ILs cover a limited number of compounds (mainly well-known ILs) at atmospheric P and a limited T range. By this reason, a number of GCMs has been reported and tested to predict IL viscosities using the available data and they are reported in Table 3.

For instance, Gardas and Coutinho (2008b) used an Orrick-Erbar-type equation (Reid et al., 1987) to predict the IL viscosity (η , cP) as follows

$$\ln \frac{\eta}{\rho \cdot W} = R_1 + \frac{R_2}{T} \quad (44)$$

where ρ (g/cm^3) is calculated from Equation (21) and the parameters R_1 and R_2 were estimated using the structural element contributions. These authors employed an experimental database with 498 viscosity values (4–21,000 cP) at 293.15–393.15 K from 29 ILs based on pyrrolidinium, pyridinium and imidazolium cations, and trifluoromethanesulfonate, ethyl sulfate, methyl sulfate, acetate, chloride, bis(trifluoromethanesulfonyl) amide, tetrafluoroborate and hexafluorophosphate anions. AARD of this model was 7.78 % with a maximum ARD value < 28 %. One drawback of this model is that requires ρ data to estimate η of ILs. This drawback was overcome by Gardas and Coutinho (2009) using a new expression based on the Vogel-Tammann-Fulcher (VTF) equation to estimate η (Pa s)

$$\ln \eta = S_1 + \frac{S_2}{(T - 165.06\text{K})} \quad (45)$$

where S_1 and S_2 were calculated by the structural element contributions s_{1i} and s_{2i} using

$$S_1 = \sum_{i=1}^k n_i s_{1i} \quad (46)$$

$$S_2 = \sum_{i=1}^k n_i s_{2i} \quad (47)$$

482 experimental data (0.004–1.065 Pa s) at 293.15–393.15 K from 25 ILs containing the next ions: trifluoromethanesulfonate, ethyl sulfate, methyl sulfate, acetate, bis[(trifluoromethyl) sulfonyl]imide, tetrafluoroborate, hexafluorophosphate, pyrrolidinium, pyridinium and imidazolium. AARD = 7.50 % and a maximum ARD value of 23 % were reported for this GCM.

The GCM proposed by Gharagheizi et al. (2012a) considers the independent anion and cation contributions to differentiate their effects on η of ILs. This GCM was formulated using an extensive database of 1672 experimental viscosity values at 250–443 K and 1 atm from 443 ILs where 46 chemical sub-structures were defined (24 for anions and 22 for cations). This database included tri-alkyl imidazolium-, tetra-alkyl imidazolium-, sulfonium-, pyrroline-, pyrrolidinium-, pyridinium-, piperidinium-, phosphonium-, oxazolodinium-, morpholinium-, isoquinolinium-, guanidinium-, double imidazolium-, ammonium-, amino acids- and imidazolium-based ILs. The next expression was used to estimate η (given in cP) of ILs

$$\log(\eta) = \sum_{i=1}^{N_a} N_{ai} U_{ai} + \sum_{i=1}^{N_c} N_{ci} U_{ci} - 0.11968T - \frac{2665.71676}{T} + 0.00013T^2 + \frac{64753.03094}{T^2} + 34.2503 \quad (48)$$

where N_{ai} and N_{ci} are the number of repetitions of the i th structural element of IL anions and cations, respectively, while U_{ai} and U_{ci} are the corresponding contributions of these elements. AARD = 6.32 % was obtained for the η estimation.

Daniel et al. (2013) proposed a GCM based on the Orrick-Erbar equation (Reid et al., 1987) to estimate η of magnetic ILs. The database included 20 experimental viscosity values (44–123,500 cP) at 293.15 – 373.15 K where this model showed AARD = 7.64 %.

Other GCM based on cation and anion contributions to estimate η of ILs was reported by Lazzús and Pulgar-Villaruel (2015). This model is given by

$$\ln \eta = 6.982 + \left(\sum_{i=1}^{N_c} N_{ci} V_{1ci} + \frac{\sum_{i=1}^{N_c} N_{ci} V_{2ci}}{T} \right) + \left(\sum_{i=1}^{N_a} N_{ai} V_{1ai} + \frac{\sum_{i=1}^{N_a} N_{ai} V_{2ai}}{T} \right) \quad (49)$$

where V_{1ci} , V_{2ci} , V_{1ai} and V_{2ai} are the contributions of the ion (cation or anion) i th. 1445 viscosity data from 6 to 20,883 cP at 253 – 395 K corresponding to 326 ILs were employed to define the model contributions. Different ILs based on isoquinolinium, oxazolodinium, morpholinium, ammonium, phosphonium, piperidinium, pyrrolidinium, pyridinium and imidazolium cations, and metal complexes, amino acid, trifluoroacetates, carboxylates, phosphates, borates, amides, imides, tosylates, sulfonates, sulfates, pseudohalides and halides anions were analyzed. This model showed AARD = 4.55 %.

The prediction of η of fluorine-containing ILs can be performed with the model of Sattari et al. (2016a) using the next expressions

$$\ln(\eta) = W_1 + W_2 \left(\frac{1000}{T} \right) + W_3 \left(\frac{1000}{T} \right)^2 \quad (50)$$

$$W_1 = \sum_{i=1}^k n_i w_{1i} \quad (51)$$

$$W_2 = \sum_{i=1}^k n_i w_{2i} \quad (52)$$

$$W_3 = \sum_{i=1}^k n_i w_{3i} \quad (53)$$

where w_{1i} , w_{2i} and w_{3i} are the structural element parameters. These parameters were obtained from the data processing of 863 viscosity values (4.1–3067.3 cP) at 258.15–388.51 K of 85 fluorine-containing ILs constituted by 58 cations and 9 anions. AARD value of 3.23 % was obtained for the η calculation with this model.

Chen et al. (2019) predicted η (Pa s) of ILs using the next equations

$$\ln \frac{\eta}{X_0} = X_1 + X_2 \frac{100}{T} + X_3 \left(\frac{100}{T} \right)^2 \quad (54)$$

$$X_1 = \sum_{i=1}^k n_i x_{1i} \quad (55)$$

$$X_2 = \sum_{i=1}^k n_i x_{2i} \quad (56)$$

$$X_3 = \sum_{i=1}^k n_i x_{3i} \quad (57)$$

where x_{1i} , x_{2i} and x_{3i} are the structural element contributions and X_0 is a model parameter. 1090 experimental data at 278–408.15 K from 76 ILs involving 8 cations, 16 anions and 3 side groups were used to define these model parameters. The performance of this model is reported in Table 3 where AARD = 3.58 % for the correlation test using all ILs with a maximum ARD value of 27.7 %.

Herein, it is convenient to highlight that the available experimental viscosity database of ILs may contain some uncertainties related to the presence of impurities in the samples employed in the quantifications and the accuracy of quantification methodologies to measure this thermodynamic property (Alcalde et al., 2015). Note that the ILs viscosity is larger than other compounds used in the industry. Therefore, these uncertainties can impact the determination of group contribution values and the corresponding model performance.

2.5. Thermal conductivity

Thermal conductivity is a transport property that measures the capability of a given material to conduct heat (Gardas and Coutinho, 2009). This property depends on the composition and chemical nature of tested compound besides the corresponding state variables like T (Lazzús, 2015). The design of thermal processes and heat transfer equipment requires the calculation of this property (Lazzús, 2015; Hosseini et al., 2019). For example, the knowledge of thermal conductivity of ILs is essential to analyze the process energy requirements including the potential phase change of ILs due to process operating conditions (Coutinho et al., 2012; Soares et al., 2019). Despite of the relevance of this thermodynamic property for process systems engineering, the available experimental information of ILs thermal conductivities is relatively limited considering the vast number of ILs that have

been synthesized (Coutinho et al., 2012; Atashrouz et al., 2016; Hosseini et al., 2019).

In particular, Gardas and Coutinho (2009) developed a GCM to estimate the thermal conductivity of ILs containing phosphonium, pyrrolidinium and imidazolium cations with chloride, ethyl sulfate, trifluoromethanesulfonate, bis(trifluoromethyl)sulfonylimide, tetrafluoroborate and hexafluorophosphate anions. They used an experimental database with 107 values (0.124–0.199 W/m K) from 16 ILs at 293–390 K. These authors proposed a linear correlation to estimate the thermal conductivity λ (W/m K)

$$\lambda = Y_1 - Y_2 T \quad (58)$$

$$Y_1 = \sum_{i=1}^k n_i y_{1i} \quad (59)$$

$$Y_2 = \sum_{i=1}^k n_i y_{2i} \quad (60)$$

where Y_1 and Y_2 were calculated using the contributions (y_{1i} and y_{2i}) of the structural elements conforming the tested IL. This GCM showed AARD = 1.06 % with a maximum ARD value of 3.5 %, see Table 4. It was extended by Gardas et al. (2010) to handle amino acid-based ILs. They used 75 experimental data ($\lambda = 0.146$ – 0.171 , W/m K) at 298–353 K from 11 amino acid-based ILs. AARD of this model was 0.67 % to predict λ for tested ILs.

Soares et al. (2019) also utilized the GCM of Gardas and Coutinho (2009) to model ILs containing 13 anion groups (e.g., FAP⁻, VAL⁻, THR⁻, TAU⁻, PRO⁻, CYS⁻, LIS⁻, SER⁻, HOPO₂⁻, CH₃COO⁻, DCA⁻, B(CN)₄⁻, C(CN)₃⁻) and recalculated the contributions for the others groups already reported. They used a database consisting of 237 experimental thermal conductivities from 0.105 to 0.214 W/m K at atmospheric P and 273–390 K from 33 ILs. This model showed AARD = 1.16 % with a maximum ARD of 4.37 %.

Wu et al. (2013) analyzed the thermal conductivity of 36 ILs composed of imidazolium, ammonium and phosphonium cations, and octylsulfate, ethylsulfate, bis(trifluoromethanesulfonyl) amide, hexafluorophosphate, tetrafluoroborate, chloride, trifluoromethanesulfonate, dicyanamide, tris(pentafluoroethyl)trifluorophosphate, acetate, tricyanomethanide, serinate, taurinate, lysinate, threonate, prolinatate and valinate anions. 25 molecular groups were used to develop the GCM via the data processing of 286 experimental values of λ (0.1050–0.2137 W/m K) at 273.15–353.15 K. This property was calculated with the next expression

$$\lambda = \sum_{j=0}^2 Z_j \left(\sum_{i=1}^k n_i \Delta z_{0i} \right)^j [1 + Z_3 (1 - T_r)^{2/3}] \quad (61)$$

where Z_j is a fixed model parameter, Δz_{0i} corresponds to the structural element contribution, T_r is obtained by Equation [9] where T_c is calculated by the GCM proposed by Valderrama et al. (2012) that is described in Section 2.12 of this review. Overall, this GCM showed low modeling errors (i.e., AARD = 1.66 %).

Albert and Müller (2014) applied a database with 372 experimental values from 39 ILs at 273.15–390 K to develop a GCM, which is given by

$$\lambda = (AA_{1cation} + AA_{1anion}) - (AA_{2cation} + AA_{2anion}) \cdot T \quad (62)$$

$$AA_{1ion} = \sum_i (v_i \cdot AA_{1i}) + AA_{1correction} \quad (63)$$

$$AA_{2ion} = \sum_i (v_i \cdot AA_{2i}) + AA_{2correction} \quad (64)$$

where AA_{1i} and AA_{2i} are the structural element contributions, $AA_{1correction}$ and $AA_{2correction}$ are additional contributions related to the type of ion or ring structure. It was reported AARD values of 2.49 % and 8.09 % for the correlation and prediction tests, see Table 4.

The GCM proposed by Lazzús (2015) estimates λ of ILs as a function of T and P (kPa) as follows

$$\lambda = \left(\sum_{i=1}^{N_c} N_{ci} AB_{1ci} + \sum_{i=1}^{N_a} N_{ai} AB_{1ai} \right) - T \left| \sum_{i=1}^{N_c} N_{ci} AB_{2ci} + \sum_{i=1}^{N_a} N_{ai} AB_{2ai} \right| + P \left| \sum_{i=1}^{N_c} N_{ci} AB_{3ci} + \sum_{i=1}^{N_a} N_{ai} AB_{3ai} \right| \quad (65)$$

where AB_{1ci} , AB_{2ci} , AB_{3ci} and AB_{1ai} , AB_{2ai} , AB_{3ai} are the contributions of i th structural element of the cations and anions, respectively. An experimental database of 400 thermal conductivities ranging from 0.1 to 0.22 W/m K at 100–20,000 kPa and 273–390 K was used. This database included thermodynamic data from 41 ILs containing ammonium, phosphonium, pyrrolidinium, pyridinium and imidazolium cations, and amino acids, acetates, phosphates, borates, imides, tosylates, sulfonates and halides as anions. ARD values of this model were < 10 % for all tested ILs. The model performance for correlation and prediction tests is reported in Table 4. Results also indicated that this GCM provided better predictions than those obtained with the models of Gardas and Coutinho (2009), Wu et al. (2013) and Albert and Müller (2014).

Finally, Oster et al. (2018) proposed alternative strategies to improve the performance of GCM of Wu et al. (2013). These strategies were based on a more accurate molecular structure characterization of ILs including the impact of cation core atom on the structure and physical properties of these compounds.

2.6. Melting point

Melting point (T_m , K) is defined as the temperature to change the physical state of a given compound from solid to liquid at atmospheric pressure (Chen et al., 2019). This thermodynamic property is essential for the calculation of vapor pressure and aqueous solubility (Katritzky et al., 2001) and it can be also employed for the chemical identification and purification (Hosseini et al., 2019). The melting points of ILs are required to characterize their phase behavior in different applications as solvents or heat transfer fluids (Aguirre et al., 2012; Mital et al., 2021). Some authors have indicated that the prediction of T_m for ILs is challenging since it depends on the arrangement of ions inside the IL crystal and their corresponding interactions (Aguirre et al., 2012; Keshavarz et al., 2018). As expected, the experimental information of ILs melting points is limited and some GCMs have been proposed for their predictions as shown in Table 5.

Huo et al. (2009) proposed a GCM to calculate T_m using 190 ILs composed of imidazolium and benzimidazolium. This model was defined as

$$T_m = \frac{\sum_k N_{Fk} AC_{1,k} + 2.355 \sum_j N_{ij} AC_{2,j}}{-0.4177 + 0.004665\alpha - 0.01859\tau + 0.005428\delta} \quad (66)$$

where N_{Fk} and N_{ij} are the frequencies of group k and ionic group j contained in the IL molecule and $AC_{1,k}$ and $AC_{2,j}$ are the melting point contributions of group k and ionic group j . Note that τ represents the number of ring groups in the

molecule, while the value of α corresponds to different scenarios: $\alpha = 1$ if the groups connected to $>NH$ and $=N-$ (ring of imidazolium) are the same, $\alpha = 0$ if different groups are connected to these structural elements. In a similar way, $\delta = 1$ if there is a group connected to the C position in the imidazolium cation and $\delta = 0$ otherwise. This model showed AARD = 5.86 % with a maximum ARD value of 32.75 %.

Lazzús (2012b) proposed a GCM to calculate this thermodynamic property for pyrazolium-, thiazolium-, morpholinium-, sulfonium-, ammonium-, phosphonium-, piperidinium-, pyrrolidinonium-, triazolium-, pyrrolidinium-, pyridinium- and imidazolium-based ILs with the following anions: metal complexes, trifluoroacetates, triflates, carboxylates, phosphates, borates, amides, imides, tosylates, sulfonates, sulfates, pseudohalides and halides. This model is defined by

$$T_m = 288.7 + \sum_{i=1}^{N_c} N_{ci}AD_{ci} + \sum_{i=1}^{N_a} N_{ai}AD_{ai} \quad (67)$$

where AD_{ci} and AD_{ai} are the contributions from the i th structural element of cations and anions, respectively. 400 ILs with T_m from 194 to 567 K were used to define the structural element contributions.

T_m of piperidinium-, phosphonium-, ammonium-, pyrrolidinium-, pyridinium- and imidazolium-based ILs can be calculated using the GCM of Aguirre et al. (2012), which is given by

$$T_m = \frac{\sum_i n_i AE_{1,i}}{0.1 + \alpha_c + 0.012\tau_c} \quad (68)$$

$$\tau_c = \sum_k (n(CH_2)_k - 1) \quad (69)$$

where $AE_{1,i}$ is the contribution of structural element i , α_c is a symmetry parameter defined for the cation and τ_c is a parameter related to the cation flexibility that is expressed in terms of the number of methylene groups (CH_2) present in the alkyl chain of IL cation minus 1. 136 ILs were analyzed with this model thus obtaining AARD = 7.8 %, see Table 5.

The following equation was employed by Gharagheizi et al. (2012c) to calculate T_m of ILs.

$$T_m = \sum_{i=1}^{N_a} N_{ai}AD_{ai} + \sum_{i=1}^{N_c} N_{ci}AD_{ci} + 264.2886 \quad (70)$$

They used an experimental database with 799 ILs containing tetra-alkyl imidazolium, tetrazolium, thiazolium, trialkyl imidazolium, triazolium, uranium, piperazinium, piperidinium, pyridazinium, pyridinium, pyrrolidinium, pyrrolidine, quinary alkyl imidazolium, morpholinium, oxazolidinium, phosphonium, sulfonium, double imidazolium, guanidinium, isoquinolinium, 1,3-dialkyl imidazolium, 1-alkyl imidazolium, amino acids and ammonium.

On the other hand, Chen et al. (2019) proposed a GCM that was formulated in terms of the number of cations (n_c), anions (n_a) and side groups (n_g) in the IL molecule and the corresponding contributions of these cations (t_c), anions (t_a) and substituents (t_g). This GCM was defined as

$$T_m = \sum_{c=1}^{k_c} n_c t_c + \sum_{a=1}^{k_a} n_a t_a + \sum_{g=1}^{k_g} n_g t_g \quad (71)$$

111 ILs were analyzed covering 3 side groups, 13 anions and 6 cation cores thus obtaining AARD = 4.7 % where the maximum modeling errors were for the calculation of tetrapropylammonium bis(trifluoromethylsulfonyl)imide IL.

Valderrama and Cardona (2021) proposed a GCM with a theoretical relationship between T_m , the melting heat (ΔH_m , kJ/mol) and the melting entropy (ΔS_m , kJ/mol·K), which was defined as

$$T_m = \frac{\Delta H_m}{\Delta S_m} \quad (72)$$

$$\Delta H_m = 3.8315 + \sum [N_{ci} \Delta H_{m,ic}] + \sum [N_{ai} \Delta H_{m,ia}] \quad (73)$$

$$\Delta S_m = 9.7736 \cdot 10^{-3} + 2.4599 \cdot 10^{-4} M_c + 1.4582 \cdot 10^{-4} M_a \quad (74)$$

$$T_m = \frac{3.8315 + \sum [N_{ci} \Delta H_{m,ic}] + \sum [N_{ai} \Delta H_{m,ia}]}{9.7736 \cdot 10^{-3} + 2.4599 \cdot 10^{-4} M_c + 1.4582 \cdot 10^{-4} M_a} \quad (75)$$

where $\Delta H_{m,ic}$ and $\Delta H_{m,ia}$ are the contributions for group i in the cation and anion, respectively, and M_c and M_a are the mass of cation and anion. AARD values of 6.47 % and 6.93 % were obtained for this model in the correlation and prediction tests.

2.7. Surface tension

Surface tension is defined as a force acting at the interface of fluid phases and it indicates the cohesive force of liquid molecules in the surface (Gharagheizi et al., 2012b; Lazzús et al., 2017b). This property affects the transfer rates of vapor absorption at the vapor-liquid interface. Therefore, it is important for the study of chemistry and physics at free surfaces and for the process design in flow and mass transfer in porous media, materials science, reactor engineering, biomedical and biochemical engineering, electronics and electrical applications (Rooney et al., 2010; Chen et al., 2019; Hosseini et al., 2019). ILs can be also used in extraction and multiphase catalytic reactions that take place at the interphase between the IL and an organic or aqueous phase and, consequently, the surface properties of ILs are required in the process analysis (Hosseini et al., 2019). Table 6 summarizes GCMs for the calculation of this property.

Gharagheizi et al. (2012b) proposed a GCM to estimate the surface tension (σ , N/m) of ILs considering the contributions of the cation (7 structural elements) and anion (12 structural elements). This model was defined as

$$\sigma = \sum_{i=1}^{N_a} N_{ai}AG_{ai} + \sum_{i=1}^{N_c} N_{ci}AG_{ci} + 0.1362154 \frac{N}{m} - 6.17 \cdot 10^{-5} \frac{N}{m \cdot T} \quad (76)$$

where AG_{ai} and AG_{ci} are the contributions of the i th structural element of anions and cations, respectively. The structural element contributions were obtained from the processing of a database containing 920 surface tension values (0.02499–0.0647 N/m) at 268.3–743.7 K from 51 ILs. Authors concluded that the accuracy of this model was acceptable with AARD = 3.61 %.

An atomic-based GCM was proposed by Shahsavari et al. (2018) to estimate σ (mN/m) of ILs at atmospheric P. In this model, the atoms usually found in ILs (e.g., iodine, boron, chlorine, bromine, fluorine, oxygen, phosphorous, sulfur, nitrogen and carbon) were selected as input parameters for the prediction of this thermodynamic property

$$\frac{\sigma}{1000} = 1.138312T^{-0.614173} + 0.007909$$

$$Nu_{Ca}^{0.150383} + 0.250221Nu_{Cc}^{-0.049454} - 0.013238$$

$$Nu_N^{0.501161} - 0.003356$$

$$(Nu_F + Nu_{Cl} + Nu_{Br} + Nu_I)^{0.092801} - 0.001367$$

$$Nu_O^{0.712848} - 0.009602Nu_S^{0.296456} - 0.005233$$

$$Nu_P^{1.068123} - 0.002497Nu_B^{0.501312} - 0.192602$$
(77)

where Nu_I and Nu_P are the number of atoms of iodine and phosphorus in the IL, respectively. This GCM was developed using 1246 surface tension data from 0.0155 to 0.0564 N/m at the melting points of 262.89–533.2 K from 61 ILs. It showed AARD values of $\sim 4.1\%$ for the correlation and prediction tests, see Table 6.

Lazzús et al. (2017b) reported a GCM to calculate σ of piperidinium-, pyrrolidinium-, pyridinium-, phosphonium-, ammonium- and imidazolium-based ILs. 2286 experimental data from 154 ILs covering a range of σ from 0.015 to 0.062 N/m at 263–533 K were used in this study. This GCM is defined by the next expression

$$\sigma = \left[\sum_{i=1}^{N_c} N_{ci} AI_{1ci} + \sum_{i=1}^{N_a} N_{ai} AI_{1ai} \right]$$

$$- T \left[\sum_{i=1}^{N_c} N_{ci} AI_{2ci} + \sum_{i=1}^{N_a} N_{ai} AI_{2ai} \right]$$
(78)

where AI_{1ci} , AI_{2ci} and AI_{1ai} , AI_{2ai} are the contributions of the i th structural element of cations and anions, respectively. This model showed AARD values of 0.07–4.03 % with a maximum ARD of 14.20 % and $R^2 = 0.91 - 0.99$ to estimate σ for these ILs. It generated lower modeling errors than those obtained with the model of Gharagheizi et al. (2012b) for small- and large-size ILs, but the performances of both models were similar for medium-size ILs.

Chen et al. (2019) proposed other GCM to calculate this IL thermodynamic property, which was defined as

$$\ln \sigma = AJ_1 + AJ_2 \left(\frac{T}{100} \right) + AJ_3 \left(\frac{T}{100} \right)^2$$
(79)

$$AJ_1 = \sum_{i=1}^k n_i a_{j_{1i}}$$
(80)

$$AJ_2 = \sum_{i=1}^k n_i a_{j_{2i}}$$
(81)

$$AJ_3 = \sum_{i=1}^k n_i a_{j_{3i}}$$
(82)

where AJ_i is calculated via the structural element contributions ($a_{j_{1i}}$, $a_{j_{2i}}$ and $a_{j_{3i}}$). 1365 surface tension data at 262.89–393 K from 102 ILs involving 6 cations, 18 anions and 2 side groups were compiled and utilized for the model development. Table 6 shows the model performance for correlation and prediction tests.

Wu et al. (2012) used an approach that combined a GCM with the corresponding-states theory (GCM-CSP) for the σ prediction of ILs containing ammonium, phosphonium, pyridinium, imidazolium, octylsulfate, methylsulfate, ethylsulfate, propylsulfate, butylsulfate, bis(trifluoromethanesulfonyl) amide, hexafluorophosphate, tetrafluoroborate, chloride, bromide, iodide, triiodide, pentaiodide, heptaoidide, nonaoidide, trifluoromethanesulfonate, dicyanamide, glutamic acid, alanine, thiocyanate, tris(pentafluoroethyl)trifluorophosphate, tetracyanoborate, trifluoroacetate and alkyltrifluoroborate ions. These authors analyzed 1224 surface tension data ranging from

15.50 to 76.20 mN/m at 268.29–533.20 K of 105 ILs. This GCM-CSP utilizes the next expression to estimate σ (mN/m)

$$\sigma = \sum_{j=0}^3 AK_j \left(\sum_{i=1}^k n_i \Delta ak_{oi} \right)^j (1 - T_r)^{11/9}$$
(83)

where Δak_{oi} are the structural element contributions and AK_j are the model parameters. Note that the value of T_c for the calculation of T_r (see Eq. (9)) can be obtained by applying the GCM proposed by Valderrama and Rojas (2009), which is described in Section 2.12 of this review. This model showed AARD = 4.95 % with a maximum ARD value of 29.92 % for [C₁₀mim][BF₄] at 293.15 K. Another model based on the parachor parameter was reported by Součková et al. (2015) to calculate σ . This approach considers the slight dependence of the parachor with respect to T and the number of carbon atoms in the cation alkyl chain.

2.8. Electrical conductivity

The capability of a given material to transport an electric charge is known as the electrical conductivity and it has been defined as the ratio of the current density to the electric field strength (Gardas and Coutinho, 2009; Chen et al., 2020). Overall, the electrical conductivity of ILs is low at room temperature but some authors have reported a substantial impact of T on this property for different ILs (Aparicio et al., 2010). The electrical conductivity of ILs is required in electrochemical applications like energy storage systems (e.g., supercapacitors, fuel cells and batteries) (Hosseini et al., 2019). Herein, it is convenient to indicate that few known ILs are suitable for electrochemical applications and, consequently, the available experimental data of this property are also limited (Chen et al., 2020). In particular, Gardas and Coutinho (2009) proposed a Vogel-Tammann-Fulcher (VTF) type equation to estimate the electrical conductivities (ε , S/m) of ILs using the next expressions

$$\ln \varepsilon = \ln AL_1 + \frac{AL_2}{T - 165.06K}$$
(84)

$$AL_1 = \sum_{i=1}^k n_i a_{l_{1i}}$$
(85)

$$AL_2 = \sum_{i=1}^k n_i a_{l_{2i}}$$
(86)

where $a_{l_{1i}}$ and $a_{l_{2i}}$ are the structural element contributions. The database of ε used by these authors covered a range of 0.01–12.68 S/m at 258.1–433.15 K with 307 experimental values from 15 ILs containing different cations (e.g., ammonium, pyrrolidinium, pyridinium, imidazolium) and anions (e.g., PF₆⁻, BF₄⁻, Tf₂N⁻, EtSO₄⁻, CF₃SO₃⁻). This model showed AARD = 4.57 % for the estimation of ε of tested ILs, see Table 7.

Wu et al. (2016) developed an alternative approach based also on VTF type equation but defining more complex group contribution equations using a second-order GCM. This model is defined as

$$\ln \varepsilon = AM_{1,j} + \frac{AM_{2,j}}{T - T_{0AM,j}}$$
(87)

$$AM_{1,j} = -2.573 + \sum_{m=1}^2 \sum_{i=1}^I n_i^m (WA_{m,i})$$
(88)

$$T_{0AM,j} = 291.166 + \sum_{m=1}^2 \sum_{i=1}^I n_i^m (WT_{0m,i}) \quad (89)$$

$$AM_{2,j} = \left(-21.452 + \sum_{m=1}^2 \sum_{i=1}^I n_i^m (WB_{m,i}) \right) \left(5.252 + \sum_{m=1}^2 \sum_{i=1}^I n_i^m (WB'_{m,i}) \right) \quad (90)$$

where $WA_{m,i}$, $WT_{0m,i}$, $WB_{m,i}$ and $WB'_{m,i}$ are the contributions of structural element i . 2195 electrical conductivity data (0.0001524 – 19.3 S/m) at 238.15–484.1 K from 188 ILs (e.g., imidazolium, phosphonium, ammonium, sulfonium, pyridinium, pyrrolidinium and piperidinium) were used to define the parameters of this model. Table 7 indicates that this GCM showed AARD = 6.02 % with a maximum ARD value of 39 % for tested ILs. Although the second-order GCMs allow to differentiate the thermodynamic properties of isomers, they require additional information about the IL molecular structures and are also more complex to be implemented due to the multi-order group subdivision.

It has been indicated that the main drawback of the model of Gardas and Coutinho (2009) relies on its limited number of contribution values that are available for the cations and anions of IL molecules. Chen et al. (2020) tried to overcome this limitation via the implementation of a GCM that can be applied for a wide spectrum of ILs. This model was developed using 1578 electrical conductivity data (0.0017–9.167 S/m) at 248.05–468.15 K of 77 ILs with 8 cations, 34 anions and 4 side groups. It is given by

$$\ln \frac{\varepsilon}{AN_0} = AN_1 + AN_2 \frac{100}{T} + AN_3 \left(\frac{100}{T} \right)^2 \quad (91)$$

$$AN_1 = \sum_{i=1}^k n_i a_{n1i} \quad (92)$$

$$AN_2 = \sum_{i=1}^k n_i a_{n2i} \quad (93)$$

$$AN_3 = \sum_{i=1}^k n_i a_{n3i} \quad (94)$$

where a_{n1i} , a_{n2i} and a_{n3i} are the structural element contributions and AN_0 is a fixed parameter given in S/m. This model showed AARD values of 3.30 % and 6.83 % for the correlation and prediction tests, see Table 7. These authors indicated that this new model outperformed the calculations with the model of Gardas and Coutinho (2009).

Finally, GCM based on LSSVM was developed by Gharagheizi et al. (2014) to estimate ε of ILs where 1077 experimental data of 54 compounds were analyzed. The performance of this model is also summarized in Table 7.

2.9. Refractive index

The refractive index (n_D) is defined as the ratio of light speed in vacuum to that obtained for another given medium (Sattari et al., 2014b). This property can be used to test the material purity, to determine a mixture concentration for certain chemical compounds, and to identify or characterize the presence of a particular substance (Gardas and Coutinho, 2009; Sattari et al., 2014b; Wang et al., 2017). n_D is associated with the intermolecular forces and their behavior in solutions and is also related with other thermodynamic properties such as the dielectric constant, surface tension and

density (Gardas and Coutinho, 2009). The experimental quantification of this property is simple but the available database covers a limited number of ILs (Sattari et al., 2014b).

To date, there are some GCMs to calculate this property for ILs (Gardas and Coutinho, 2009; Freire et al., 2011; Soriano et al., 2010b; Almeida et al., 2013; Sattari et al., 2014b; Wang et al., 2017), see Table 8. For instance, Gardas and Coutinho (2009) proposed the next GCM for the calculation of n_D of ILs composed of imidazolium with PF_6^- , BF_4^- , Tf_2N^- , $MeSO_4^-$, $EtSO_4^-$, $CF_3SO_3^-$ and Cl^- anions at 283.15–363.15 K

$$n_D = AO_1 - AO_2 T \quad (95)$$

$$AO_1 = \sum_{i=1}^k n_i a_{o1i} \quad (96)$$

$$AO_2 = \sum_{i=1}^k n_i a_{o2i} \quad (97)$$

where a_{o1i} and a_{o2i} are the structural element contributions. 245 experimental data from 24 ILs were used to develop this model, which showed AARD = 0.18 % where a maximum ARD of 0.61 %.

This model was also employed by Freire et al. (2011) to calculate n_D of ILs containing 1-ethyl-3-methylimidazolium cation and dimethylphosphate, tosylate, thiocyanate, dicyanamide, trifluoromethanesulfonate, methanesulfonate, methylphosphonate and acetate anions. These authors recalculated the structural element contributions and proposed new values for other elements not included in the original model. Other variants of this GCM were proposed by Soriano et al. (2010b) and Almeida et al. (2013). Sattari et al. (2014b) reported other alternative model to estimate this property, which is given by

$$n_D = AP_1 + AP_2 T \quad (98)$$

$$AP_1 = 1.5082 + \sum_{i=1}^k n_i a_{p1i} \quad (99)$$

$$AP_2 = -1.4207 \cdot 10^{-4} + \sum_{i=1}^k n_i a_{p2i} \quad (100)$$

where a_{p1i} and a_{p2i} are the structural element contributions that were obtained from the processing of a database with 931 experimental values ranging from 1.3551 to 1.5778 at 283–363.15 K. This database included 97 ILs of different families (e.g., amino acid, ammonium, imidazolium, phosphonium, pyridinium, pyrrolidinium) constituted by 50 cations and 33 anions. The model performance is also described in Table 8.

Wang et al. (2017) employed 2138 experimental data at 283.15–368.15 K of 299 ILs to obtain the structural element contributions for the prediction of this property in ILs. These contributions covered pyrazolium-, piperidinium-, sulfonium-, guanidinium-, pyrrolidinium-, amino acid-, phosphonium-, ammonium-, pyridinium- and imidazolium-based ILs, which can be represented by 9 cations, 9 anions and 23 substituents attached to the cores. This GCM was established as

$$n_D = \left(1.4626 + \sum_{i=1}^k n_i a_{q1i} \right) + 0.02372 \frac{T}{100} \quad (101)$$

where a_{q1i} is the contribution of structural element i . The performance of this model was also acceptable for

correlation and prediction tests, see Table 8, with AARD = 0.628 % and $R^2 = 0.89$.

2.10. Thermal decomposition temperature

The thermal decomposition temperature is related to the thermodynamic stability of compounds (Keshavarz et al., 2016a). ILs are nonvolatile and, consequently, the thermal decomposition temperature establishes the upper limit of T for their existence as liquid and their corresponding application as solvents in chemical processes (Lazzús, 2012c; Gharagheizi et al., 2013; Mokadem et al., 2016). Therefore, this property and the melting point can be used to define the operation limits of ILs-based processes (Mokadem et al., 2016). Overall, ILs have high thermal stabilities and can operate over a wide T range because these compounds usually decompose at > 300 °C (Lazzús, 2012c). In terms of the modeling of this property, Lazzús (2012c) proposed a GCM to calculate the thermal decomposition temperature (T_d , K) of ILs containing thiazolium, pyrazolium, triazolium, oxazolidinium, morpholinium, ammonium, phosphonium, piperidinium, pyrrolidinium, pyridinium and imidazolium cations, and metal complexes, amino acids, trifluoroacetates, carboxylates, phosphates, borates, amides, imides, tosylates, sulfonates, sulfates, pseudohalides and halides as anions. This model was defined by

$$T_d = 663.85 + \sum_{i=1}^{N_c} N_{ci}AR_{ci} + \sum_{i=1}^{N_a} N_{ai}AR_{ai} \quad (102)$$

where AR_{ci} and AR_{ai} are the contributions of the structural elements from cations and anions, respectively. This model was assessed using an experimental database with T_d (403 – 857 K) of 198 ILs. It showed AARD = 4.28 % to estimate T_d with a maximum ARD value of 25.7 %, see Table 9.

GCM of Gharagheizi et al. (2013) can be applied to calculate this property for uranium-, triazolium-, tri-alkyl imidazolium-, tetrazolium-, tetra-alkyl imidazolium-, sulfonium-, quinary alkyl imidazolium-, pyrrolidinium-, pyridinium-, pyridazinium-, piperidinium-, phosphonium-, oxazolidinium-, morpholinium-, guanidinium-, double imidazolium-, ammonium-, amino acids-, 1-alkyl imidazolium- and 1,3-dialkyl imidazolium-based ILs. These compounds included 58 anions and 313 cations that can be divided into 30 structural elements (i.e., 20 cation structural elements and 10 anion structural elements). This GCM is defined as

$$T_d = \sum_{i=1}^{10} N_{ai}AS_{ai} + \sum_{i=1}^{20} N_{ci}AS_{ci} + 524.5031 \quad (103)$$

where AS_{ai} and AS_{ci} are the contributions for T_d of the i th structural element of anions and cations. The contributions of this model were obtained from experimental data of 613 ILs with $T_d = 374 - 740$ K. Table 9 summarizes the model performances for the correlation and prediction tests.

Mokadem et al. (2016) proposed a high-order GCM to calculate T_d of ILs using the next expression

$$T_d = 647.492 + \sum_l n_l AT_{2l} + \sum_k m_k AT_{3k} - 78.576AT_0 \quad (104)$$

where n_l and m_k are the number of first and second-order groups of the type l and k , respectively and AT_{2l} and AT_{3k} are the corresponding group-interaction contributions. The third order contribution is a correction term that incorporates the equivalent number (AT_0) and depends on the IL under analysis. 639 experimental T_d data of ILs were used to define the

model parameters. These ILs included the next cations: amino acids, caprolactam, butyrolactam, benzotriazolium, oxazolidinium, ammonium, morpholinium, sulfonium, pyrrolidinium, piperidinium, phosphonium, pyrimidine, guanidinium, tetrazolium, pyridinium, triazolium and imidazolium. The anions included dinitramide, sulfonate, borate, sulfonate, azide, perchlorate, nitrate, 5-nitrotriazolate, 4,5-dinitroimidazolate, 3-nitro-1,2,4-triazolat, dicyanamide, tricyanomethanide, tris (trifluoromethylsulfonyl) methide, trifluoromethylsulfonate, trifluoroacetate, bis(trifluoromethylsulfonyl)imide, halide, alkylsulfate, carboxylates, dialkylphosphate, tetrafluoroborate and hexafluorophosphate. It was concluded that this model estimated T_d of ILs with low prediction errors, see Table 9.

2.11. Normal boiling point

Normal boiling point is a relevant property for the application of ILs. This thermodynamic property can be defined as the temperature where the vapor pressure of a liquid is equal to 1 atm (Deng et al., 2016). This property is used as input variable for several correlations and predictive thermodynamic models to estimate the solubility, vapor pressure and critical properties of pure compounds (Valderrama and Robles, 2007; Valderrama et al., 2008, 2012, 2015; Admire et al., 2015). The experimental determination of the normal boiling point of ILs is restricted by their thermal decomposition temperature where several ILs can degrade at temperatures approaching their normal boiling points (Valderrama and Robles, 2007).

The prediction of this property can be performed with GCM proposed by Valderrama and Robles (2007). They modified the model of Valderrama and Venegas (2004), which was based on Lydersen-Joback-Reid approach, to estimate the normal boiling point (T_b , K) of 50 ILs. This model is given by

$$T_b = 198.2 + \sum_i n_i \Delta T_{bi} \quad (105)$$

where ΔT_{bi} is the contribution of the structural element i of IL molecule. Note that the estimations obtained with this model were not directly validated because of the lack of experimental data of T_b for several ILs. Therefore, these authors tested the model accuracy via the calculation of ρ of ILs using a generalized correlation proposed by Valderrama and Abu-Sharkh (1989), which only needs the values of T_b , W and critical properties of tested IL molecules as input variables. The maximum value of ARD was 19.3 % using this validation test. The authors stated that the estimations obtained with this GCM were proper to perform engineering calculations using EoS. This model was later extended for 200 ILs (Valderrama et al., 2008) and was also revised to recalculate the group contribution values and incorporating new groups (Valderrama and Rojas, 2009).

Valderrama et al. (2012) updated the studies performed by Valderrama and Robles (2007), Valderrama et al. (2008) and Valderrama and Rojas (2009) where T_b of 1130 ILs were reported. These authors also introduced a new and complementary consistency test based on the calculation of ILs saturation pressure at T_b with a cubic EoS (Valderrama et al., 2012). The model performance for consistency tests based on ρ and vapor pressure are shown in Table 10.

In other study, Valderrama et al. (2015) extended their GCMs to handle ILs with a molar mass > 500 g/mol where 316 compounds were considered. Another extension of these

models was proposed by Valderrama et al. (2019) for ILs containing metals where the group contribution values of 29 new metal groups were reported. A computer tool was recently reported by Valderrama et al. (2021) using the Lydersen GCM (Lydersen, 1955) to calculate this IL property. Table 10 summarizes the performances of these GCMs. This table also reports the performance of GCMs that have been combined with a fragment contribution approach and the corresponding states method (Huang et al., 2013) and the Patel-Teja EoS (Shen et al., 2011) for the calculation of T_b of ILs.

2.12. Critical properties

Critical properties (i.e., volume V_c , pressure P_c , temperature T_c) characterize the vapor-liquid phase behavior of pure components (Tahami et al., 2019). They are used as input variables to identify their chemical nature during process design calculations with thermodynamic models like cubic EoS and to estimate other thermodynamic properties (e.g., density, viscosity, enthalpy, heat capacity, heat of vaporization, vapor pressure, thermal conductivity) (Valderrama et al., 2012). Formally speaking, T_c and P_c of the pure component are the conditions where the properties of its liquid and gas phases are the same because the phase boundaries disappear and, consequently, they cannot be differentiated from each other, while V_c is the corresponding volume of this substance at these thermodynamic conditions (Tahami et al., 2019). There is a limited number of experimental data of critical properties of ILs since several compounds can decompose before reaching the critical point (Valderrama and Robles, 2007). Therefore, the prediction of critical properties of ILs is fundamental to support the design, optimization, modeling and control of different processes. Table 10 summarizes GCMs to calculate the critical properties of ILs.

Valderrama and Robles (2007) proposed a modified version of the Lydersen-Joback-Reid GCM to estimate T_c (K), P_c (bar) and V_c (cm^3/mol) of ILs as follows

$$T_c = \frac{T_b}{0.5703 + 1.0121 \sum n \Delta T_M - (\sum n \Delta T_M)^2} \quad (106)$$

$$P_c = \frac{W}{[0.2573 + \sum n \Delta P_M]^2} \quad (107)$$

$$V_c = 6.75 + \sum n \Delta V_M \quad (108)$$

where ΔT_M , ΔP_M and ΔV_M are the structural element contributions for the calculation of T_c , P_c and V_c , respectively. These authors highlighted that the estimations of the critical properties obtained with this GCM could not be directly validated for some ILs due to the lack of experimental data. They proposed to perform a density test to assess the model accuracy. This GCM has been utilized to model IL-based processes using different EoS (Carvalho et al., 2009, 2010) and to calculate other properties based on the corresponding states theory (Ge et al., 2008; Valderrama and Zarricueta, 2009). Some updates of this model were reported by Valderrama et al. (2008) and Valderrama and Rojas (2009) where more ILs and structural elements were included and the contribution values were also recalculated.

Valderrama et al. (2012) proposed a new consistency test based on the calculation of the saturation pressure to complement the density test thus including the validation of T_c , P_c , ω and T_b . Other variants of this model were proposed for

handling ILs with molecular mass > 500 g/mol (Valderrama et al., 2015) and for ILs containing metals where 29 new metal groups were incorporated (Valderrama et al., 2019).

An approach based on the concepts of the fragment contribution and corresponding states (FC-CS) was proposed by Huang et al. (2013) to estimate the critical properties of ILs. The fragment contribution consists of the division of ILs into fragments: cation fragment, anion fragment and substituent fragment attached to the cation or anion. Other model based on the Patel-Teja EoS and GCM of Valderrama and Robles (2007) (GC-PT) was reported by Shen et al. (2011) to predict the critical properties of ILs. Sattari et al. (2016b) applied GCM and QSPR to estimate T_c of ILs. These authors analyzed the limitations of some GCMs to predict the critical properties of ILs.

Recently, Valderrama et al. (2021) published a simple computer tool based on different approaches (e.g., GCMs, semi-empirical correlations, EoS) to calculate several properties of ILs including critical properties. These authors implemented their GCMs and some improved variants where the consistency tests (density and vapor pressure tests) have been also utilized.

Finally, the results reported in the literature indicated that available GCMs show high modeling errors to estimate the critical properties of some ILs, which fundamentally relies on the lack of experimental information to define proper values of model contributions. However, the accuracy of these models can be improved using alternative numerical tools as will be discussed in this review.

2.13. Other thermodynamic properties

Different GCMs have been introduced for the calculation of other thermodynamic properties of ILs that are required in process systems engineering. They include the freezing point (Lazzús, 2016a), isobaric expansivity (Gardas and Coutinho, 2009), isothermal compressibility (Gardas and Coutinho, 2009) and static dielectric constant (Zhou et al., 2014). These properties have been estimated using GCMs and some of them are briefly described below where Table 11 summarizes their numerical performances.

For instance, the freezing point is the temperature where a liquid phase changes to a solid state (Lazzús, 2016a). Theoretically, this temperature should be the same as the melting point of a solid but, for the case of ILs, significant differences between these values have been observed (Lazzús, 2016a). A peculiar characteristic of ILs is that they display a substantial supercooling at relatively high T (Hosseini et al., 2019). ILs tend to form crystals during the cooling when they present a freezing transition. For these cases, ILs should be submitted a faster cooling to avoid the crystallization during a freezing transition (Lazzús, 2016a). The experimental determination of freezing point of ILs is difficult due to this type of transition could occur over a wide range of T and also depends on P (Lazzús, 2016a). Lazzús (2016a) proposed a GCM to predict the freezing point of ILs. This model was developed using experimental data of freezing point temperatures from 185 to 466 K of 63 ILs. This model was based on the definition of 10 cation groups (e.g., ammonium, phosphonium, pyrrolidinium, pyridinium and imidazolium) and 21 anion groups (e.g., metal complexes, carboxylates, phosphates, borates, imides, tosylates, sulfonates, pseudohalides and halides). The next equation can be used to estimate the IL freezing point (T_f , K)

Table 12 – Different GCM-ANN approaches for the estimation of thermodynamic properties of ILs.

Model	Property	Modeling performance ¹				Remarks
		N _{IL}	N _{dat}	AARD, %	R ²	
Valderrama et al. (2009)	Density	103	399	0.15	N/A	Correlation set
		24	82	0.26	N/A	Prediction set
Lazzús (2009b)	Density	164	2162	0.44	0.99	Global set
		131	1736	0.43	0.99	Correlation set
Lazzús (2009a)	Density	33	426	0.49	0.99	Prediction set
		322	3183	0.55	N/A	Global set
		250	2410	0.57	0.99	Correlation set
Paduszyński and Domańska (2014)	Viscosity	72	773	0.48	0.99	Prediction set
		1484	12,405	11.4	0.98	Global set
		41	400	0.89	0.99	Global set
Lazzús (2016b)	Thermal conductivity	30	300	0.91	0.99	Correlation set
		11	100	0.84	0.99	Prediction set
		162	2307	1.18	0.99	Global set
Lazzús et al. (2017a)	Surface tension	108	1728	1.17	0.99	Correlation set
		54	579	1.29	0.99	Prediction set
		299	2138	0.18	0.96	Global set
Wang et al. (2017)	Refractive index	277	1711	0.17	0.97	Correlation set
		190	427	0.22	0.93	Prediction set

¹ Variable description:
N_{IL}: Number of ILs used in the study.
N_{dat}: Number of experimental data analyzed in the study.
R²: Coefficient of determination.
N/A: Data not available.

$$T_f = 98.599 + \sum_{i=1}^{10} N_{ci}AU_{ci} + \sum_{j=1}^{21} N_{aj}AU_{aj} \quad (109)$$

where AU_{ci} and AU_{aj} are the contributions of the i th structural element that conformed the cations and anions, respectively.

The isobaric expansivity is required to perform calculations related to the volumetric behavior of ILs and their changes with respect to state variables (Gardas and Coutinho, 2009). This thermodynamic property is utilized for the analysis of heat transfer fluids and energy storage. Gardas and Coutinho (2009) reported a GCM to calculate this property, which was formulated via the analysis of 109 isobaric expansivity data ($\alpha_p = 4.48 \cdot 10^{-4} - 7.44 \cdot 10^{-4} \text{ K}^{-1}$) at 298.15 K and 0.1 MPa from 49 ILs. This model covered ILs conformed of ammonium, phosphonium, piperidinium, pyrrolidinium, pyridinium and imidazolium. The isobaric expansivity (α_p , K^{-1}) of ILs can be determined with the next expression

$$\alpha_p = AV_1 = \sum_{i=1}^k n_i av_{1i} \quad (110)$$

where av_{1i} corresponds to the structural element contributions of this model.

The isothermal compressibility is utilized in fluid dynamics and design like the analysis of compressors and pumps (Hosseini et al., 2019). It has been defined as a measure of the relative volume change of a fluid with respect to P at fixed T (Gardas and Coutinho, 2009). Gardas and Coutinho (2009) introduced a GCM to estimate the isothermal compressibility (k_T , GPa^{-1}) of ILs at $0.33 - 0.73 \text{ GPa}^{-1}$ using the next equation

$$k_T = AW_1 = \sum_{i=1}^k n_i aw_{1i} \quad (111)$$

where aw_{1i} is the contribution of structural element i . These contributions were determined from the data processing of 26 experimental values at 298.15 K and 0.1 MPa from 22 ILs

containing phosphonium, piperidinium, pyrrolidinium, pyridinium and imidazolium.

Finally, the static dielectric constant is required to estimate the electro-viscous effect that occurs when fluids with ions flow in microdevices like microreactors, micropumps and microheat exchangers (Zhou et al., 2014). This property is also a measure of the polarity and solvation capabilities of ILs (Zhou et al., 2014). Few studies have reported static dielectric constant of some ILs (Zhou et al., 2014). The estimation of ILs static dielectric constants (κ) can be performed with the GCM of Zhou et al. (2014), which is given by

$$\kappa = \frac{3}{1 - \frac{AX}{W\rho}} - 2 \quad (112)$$

$$AX = \sum_{i=1}^k n_i ax_i \quad (113)$$

where ax_i represents the structural element contributions of this model. These authors applied a database of 128 experimental at 278.15 – 343.15 K from 58 ILs to determine the corresponding model parameters.

2.14. Estimation of thermodynamic properties using hybrid models from GCM and artificial neural networks

GCMs have some drawbacks for the prediction of physico-chemical properties of some ILs with a complex thermodynamic behavior. For example, the viscosity and melting point of ILs are more difficult to predict using only simple structural information of the molecule. As a consequence, the classical GCMs can provide poor estimations for these thermodynamic variables (Hosseini et al., 2019). For these challenging calculations, the ANN can be utilized to improve the model performance and to develop enhanced predictive models.

ANN is a family of statistical learning efficient algorithms that allows to model challenging non-linear behaviors

(Lazzús, 2009a; Wang et al., 2017). This numerical tool is based on imitating the complex operation of the biological nervous systems (Fatehi et al., 2014). For interested readers, a detailed description of ANN is provided in the reviews of Abiodun et al., (2018, 2019).

The basis of GCM have been integrated with ANN to develop a new class of thermodynamic models (GCM-ANN) for the estimation of thermodynamic properties of ILs. Some of these models are described in Table 12. For example, Valderrama et al. (2009) used a hybrid GCM-ANN model to estimate IL densities. The results indicated that this model predicted the IL density with an acceptable accuracy for engineering calculations. Padaszyński and Domańska (2014) developed a hybrid GCM-ANN model to calculate ILs viscosities. The model performance was substantially better than that of the model of Gardas and Coutinho (2009) to estimate the viscosities of different types of ILs. This model can be applied for predicting the properties of more ILs compared to other models reported in the literature. In these hybrid models, the molecules are generally divided into their structural elements, but instead of using an explicit mathematical expression to define the functionality of these contributions, the ANN is trained to learn the relationship between the input variables (i.e., structural elements that conform the IL molecule including other parameters like the molar mass, temperature, pressure) and the corresponding output variables that are the desired property for the set of analyzed compounds.

3. Conclusions and perspectives of GCMs for ionic liquids property calculations

This review has covered a wide spectrum of GCMs for the prediction of thermodynamic properties involved in the process systems engineering. The analysis of model performance suggested that some GCMs have been obtained from databases with a limited number of experimental values thus generating that they could not be employed to predict the properties of different ILs for the case of novel molecules. For some operating conditions, the errors of GCMs to predict some ILs thermodynamic properties could be relatively significant to carry out a proper process design and simulation. It appears that the more challenging IL properties to be estimated correspond to the critical temperature and pressure, while the heat capacity and density are the properties more analyzed and studied for ILs where different GCMs can be used for their calculation. Although high order GCMs may offer better results for the IL property calculations, they require more detailed information of IL molecules and additional parameters. Under this scenario, the first-order GCMs should be the first and straightforward option for the prediction of ILs thermodynamic properties but additional efforts are required to reduce their modeling errors especially for those properties that have been not extensively studied in the literature.

The improvement of GCMs for obtaining reliable thermodynamic calculations of ILs should be cover some of the next key issues:

- a) As stated, the contributions of structural elements that compose the ILs molecules are obtained from the experimental data processing. For some ILs properties, the available experimental values are limited or can contain significant uncertainties. Consequently, it is convenient to review and recalculate the model contributions of available GCMs via the incorporation of new experimental information that has been reported during the last years. Also, it is necessary to establish experimental working plans to expand the number of ILs and their properties as well as to quantify novel and well-known compounds but at different operating conditions. This aspect is fundamental for creating a ILs database with a vast quantify of experimental values to develop reliable GCMs for the calculations required in process systems engineering.
- b) An in-deep analysis of the effect of type of cations and anions conforming the molecular structure of ionic liquids on the prediction of their thermodynamic properties is necessary and should be performed in forthcoming studies. To the best of authors knowledge, this analysis has not been reported in the literature for the thermodynamic properties of ionic liquids. Since some estimations have indicated that around 10^6 possible ionic liquids can be synthesized, the results of this analysis can contribute to define molecular structure – property relationships with the aim of understanding the thermodynamic behavior of these compounds and to improve the prediction capabilities of GCMs.
- c) Several authors have applied local optimization methods to resolve the parameter estimation problems involved in the determination of structural element contributions of CGMs. However, these multivariable parameter identification problems are challenging and imply potential non-convex objective functions. So, global optimization solvers should be applied to minimize the corresponding objective functions with the aim of identifying the best model parameters. In this direction, the application of novel stochastic optimization methods is an interesting alternative.
- d) It seems clear that ANN can improve the performance of GCMs for the calculation of ILs thermodynamic properties. Several advances and improvements of ANN have reported during the last decades thus opening the possibility of applying improved ANN approaches to enhance the capabilities of thermodynamic models based on GCM. Also, other artificial intelligence tools can be tested and categorized to identify the best one for the calculation of a specific thermodynamic property.

GCMs represents an effective approach to support the computer-aided process design of novel processes and operation units based on ILs but it is mandatory to improve their performance for obtaining reliable estimations of performance metrics like separation efficiencies, energy requirements, costs and other relevant metrics utilized in the decision-making stage.

CRedit authorship contribution statement

V. Villazón-León: Writing – original draft, Conceptualization, Methodology, Investigation. Adrián Bonilla-Petriciolet: Writing – review & editing, Investigation, Supervision, Project administration. J.C. Tapia-Picazo: Writing – review & editing, Investigation, Supervision. J.G. Segovia-Hernández: Writing – review & editing, Investigation. M.L. Corazza: Writing – review & editing, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cherd.2022.07.033.

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