Theoretically consistent calculation of viscous activation parameters through the Eyring equation and their interpretation

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ABSTRACT

The activation parameters of viscous flow can be used to probe the molecular interactions in fluids from viscosity experimental data. They are assessed by mathematical derivations of the Eyring equation, but differences in these derivations can generate parameters that lead to conflicting interpretations. In this work, a new method for the estimation of the activation parameters of viscous flow is proposed and compared with two other methods previously reported in the literature. It is shown that the new method is the only presenting theoretically consistent trends, as confirmed by its application to alkanes and ionic liquids.

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1. Introduction

The determination of both thermodynamic and transport properties of solutions is essential to understand the behavior of liquid mixtures. Density, viscosity, sound velocity, refractive index, surface tension and dielectric constant are key parameters [1]. Among them, viscosity has a considerable interest as simple to assess, yet relevant property due to its influence on other transport properties such as mass and heat transfer, essential in many chemical processes, including mixing, stirring, chemical reactions and separation processes [2–4].

There are two main interests in studying viscosity. Firstly, obtaining experimental data is important to establish the process operational conditions. Then, viscosity can provide information on a molecular basis since it is a direct consequence of intermolecular interactions [5]. One way to understand intermolecular interactions from viscosity is by determining the thermodynamic activation parameters of viscous flow through the Eyring equation [6], namely Gibbs energy $\Delta G^{\ddagger}$, enthalpy $\Delta H^{\ddagger}$, entropy $\Delta S^{\ddagger}$, and the variation of calorific capacity $\Delta C_P^{\ddagger}$. An old theory developed by Eyring and co-workers [7] provides a qualitative interpretation of the viscous flow process and allows a rough estimatation of the viscosity from other physical properties.

Several studies report the use of this equation to determine the activation parameters of the viscous flow. In general, viscosity parameters are studied for binary mixtures, with the parameters considered a function of composition, and independent of temperature [5,8–15]. Some studies use this approach to understand the intermolecular interactions that occur in pure substances [2,4,16,17]. For the estimation of activation parameters for pure compounds, there is more than one calculation methodology leading to conflicting results.

The understanding of molecular interactions is particularly important for complex substances such as ionic liquids (IL). These are liquids composed entirely by ions [18] in which the electrostatic interactions may no longer be dominant but instead coexist with hydrogen bonding, polar interactions and dispersion forces, making the intermolecular interaction on these fluids very rich and complex. ILs are known for having interesting properties and, thanks to the strong interactions between their ions, they possess relatively high viscosities [3,19], which may be an advantage for some applications as lubrication, however, a problem for chemical processes involving heat and mass transfer [4].

One of the most exciting properties of ILs is their tunability, i.e., by changing cations and anions, a wide range of physical properties such as hydrophobicity, density and viscosity may be modulated, allowing the design of ionic liquids for specific applications [19–22]. For instance, depending on the chemical structure, ILs

Nomenclature

Parameters

a, b, c	polynomial parameters adjusted for quadratic polynomial (Method 1)
A, B	fitting parameter of Litovitz equation
A', B'	fitting parameters of VFT equation
a', b'	fitting parameters of Ghatee equation
h	Planck constant
N_A	Avogadro constant
P	pressure
R	universal gas constant
T	temperature
T_0	glass transition temperature
V_m	molar volume

Greek symbols

$\Delta C_P^{\ddagger}$	variation of calorific capacity of activation
$\Delta G^{\ddagger}$	Gibbs energy of activation
$\Delta H^{\ddagger}$	enthalpy of activation
$\Delta S^{\ddagger}$	entropy of activation
η	dynamic viscosity
ρ	density
φ	characteristic exponent

Ionic liquids acronyms

[Bmim][BF4]	1-butyl-3-methylimidazolium tetrafluoroborate
[Bmim][PF$_6$]	1-butyl-3-methylimidazolium hexafluorophosphate
[Emim][EtSO$_4$]	1-ethyl-3-methylimidazolium ethylsulfate
[Emim][NTf$_2$]	1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide
[Bmim][NTf$_2$]	1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide
[N4111][NTf2]	butyltrimethylammonium bis(trifluoromethyl- sulfonyl)imide
2-HDEAA	2-hydroxy diethylammonium acetate
2-HEAPr	2-hydroxy ethylammonium propionate
2-HDEAL	2-hydroxy diethylammonium lactate
2-HEAL	2-hydroxy ethylammonium lactate
2-HEAA	2-hydroxy ethylammonium acetate

viscosity may vary from as low as octanol to as high as tomato paste [3]. This complex behavior turns into a challenge the understanding of ILs molecular interactions and the prediction of their physical properties.

The objective of this work was to evaluate the intermolecular interactions present in ionic liquids by assessing the activation parameters of their viscous flow using the Eyring equation. Two methodologies, available in the literature, for calculating the activation parameters from viscosity experimental data were tested and proved unsatisfactory, prompting us to derive a new methodology that was here applied to simple substances (alkanes containing 5 to 12 carbons) and to aprotic and protic ILs.

2. Methodology

The thermodynamic activation parameters $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta C_P^{\ddagger}$ were estimated from the Eyring equation (Eq. (1)).

$$\eta = \frac{hN_A}{V_m} \exp\left(\frac{\Delta G^{\ddagger}}{RT}\right) \tag{1}$$

where η is the dynamic viscosity, h is the Planck constant, N_A is the Avogadro constant, V_m is the molar volume, R is the universal gas constant, and T is the absolute temperature. From the definition of $\Delta G^{\ddagger}$:

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \tag{2}$$

The viscosity can be expressed in terms of Eq. (3):

$$\ln \eta = \ln\left(\frac{hN_A}{V_m}\right) + \frac{\Delta H^{\ddagger}}{RT} - \frac{\Delta S^{\ddagger}}{R} \tag{3}$$

The most common models to describe the temperature dependence of viscosity are Litovitz and Vogel-Fulcher-Tamman (VFT). Many studied have shown that the Arrhenius equation is not suitable for describing viscosity of IL, which presents a very sharp increase at low temperatures and a smooth decrease at high temperatures [23–25], excepting when applying to small ranges of temperature [26]. Litovitz equation fits the viscosity of non-Arrhenius fluids with acceptable accuracy; however, it presents parameters that do not adhere to physical meaning [27]. VFT equation parameters, on the other hand, includes the glass transition temperatures, T_0 in the exponential term [14,27,28]. The Litovitz and VFT equations are given according to Eqs. (4) and (5).

$$\eta = A \exp(B/RT^3) \tag{4}$$

$$\eta = A' \exp\left(B'/(T - T_0)\right) \tag{5}$$

where A, B, A' and B' are fitting parameters; and B' is related to the free energy of activation.

More recently, Ghatee and co-workers [25] developed a simple linear equation based on the fluidity concept ($1/\eta$), as it shows a smoother relation with temperature, especially for high viscosity fluids. Ghatee equation (Eq. (6)) has been successfully used to describe the viscosity of ILs [2,16,27,29].

$$\left(\frac{1}{\eta}\right)^{\varphi} = a'T + b' \tag{6}$$

where a' and b' are substance dependent constants, the characteristic exponent φ equal to 0.3 is suitable for several IL [25].

Interestingly, besides the knowledge of all those empirical relations to describe viscosity data, the activation parameters are being determined in the literature by adjusting experimental data to quadratic polynomials [2,16,30] or linear relations [11,13], considering only the shape of the curves of the plot $\ln \eta$ versus T, leading to physically inconsistent values, and the use of viscosity empirical models overcome this problem, as further explored following.

2.1. Method 1

The method 1 was first used by Mukherjee et al. [30] and has been used by several other authors to describe the viscosity of various IL, including protic [2], and aprotic ILs [16,17,31]. In this methodology, experimental viscosity data were adjusted to Eq. (7) [2,16,17]:

$$\ln \eta = aT^2 + bT + c \tag{7}$$

The choice was made considering the shape of the plot $\ln \eta$ versus T [2,16,31]. The term $\ln\left(\frac{hN_A}{V_m}\right)$ becomes independent of temperature, disregarding the linear relation of V_m with temperature and, thus, applicable only in limited conditions such as for condensed states, low pressures and narrow temperature ranges. Thus, deriving Eq. (7) in relation to temperature, Eq. (8) was obtained [2,16,30]:

$$\left(\frac{\partial \ln \eta}{\partial T}\right)_P = -\frac{\Delta H^{\ddagger}}{RT^2} = (2aT + b) \tag{8}$$

$\Delta C_P{}^{\ddagger}$ is obtained from its definition (Eq. (9)):

$$\Delta C_P{}^{\ddagger} = \left(\frac{\partial \Delta H^{\ddagger}}{\partial T}\right)_P = -2RT(3aT + b) \tag{9}$$

$\Delta G^{\ddagger}$ is obtained from Eq. (1) and $\Delta S^{\ddagger}$ by the fundamental thermodynamic relationship (Eq. (2)). The works carried by Andrade et al. [16] and Camargo et al. [2] demonstrated that Ghatee, Litovitz and VFT equations were able to describe the viscosity of IL satisfactorily, and yet the authors used a quadratic polynomial (Eq. (7)) to fit viscous activation parameters.

2.2. Method 2

Several authors have widely adopted this approach proposed by Kapadi et al. [13] for estimation of activation parameters of binary mixtures, including aqueous solutions of ILs [11], propane-1,2-diol [13] and ethylene diamines [14]. In Method 2, Eq. (3) is rewritten as:

$$\ln\left(\frac{\eta V_m}{h N_A}\right) = \frac{\Delta H^{\ddagger}}{RT} - \frac{\Delta S^{\ddagger}}{R} \tag{10}$$

With $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ being considered constant with temperature. $\Delta H^{\ddagger}/R$ is the slope and $-\Delta S^{\ddagger}/R$ is the intercept of the plot $\ln\left(\frac{\eta V_m}{h N_A}\right)$ vs $1/T$. Since $\Delta H^{\ddagger}$ is constant, $\Delta C_P{}^{\ddagger}$ is zero and $\Delta G^{\ddagger}$ is obtained by its definition (Eq. (2)).

2.3. Method 3

Method 3 is an improvement of the methodologies described above. In this method, the molar volume, enthalpy, and entropy are all considered to be temperature dependent. Thus, Method 3 is more generic than the previous, removing the constraints of these methods, and can be safely applied in broader ranges of temperature. $\Delta G^{\ddagger}$ is obtained isolating the term from the Eyring equation (Eq. (1)). $\Delta H^{\ddagger}$ is obtained by using the Gibbs-Helmholtz equation (Eq. (11)).

$$\Delta H^{\ddagger} = \left(\frac{\partial\left(\Delta G^{\ddagger}/T\right)}{\partial\left(1/T\right)}\right)_P \tag{11}$$

Thus, the enthalpy of activation $\Delta H^{\ddagger}$ is calculated by the derivation of function $\Delta G^{\ddagger}/T$ with respect to $1/T$. Specific heat of activation $\Delta C_P{}^{\ddagger}$ is given by the derivation of the activation enthalpy $\Delta H^{\ddagger}$ in relation to temperature. The activation entropy $\Delta S^{\ddagger}$ is obtained from its thermodynamic definition (Eq. (2)). The viscosity

may be described by any of before mentioned empirical models for describing viscosity.

3. Results and discussion

3.1. Evaluation of the methodologies

To evaluate the various methodologies available for the estimation of the thermodynamic activation parameters $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta C_P{}^{\ddagger}$ described in the previous section, the ionic liquid [Bmim][BF$_4$] was adopted. An ionic liquid was chosen due to the complex interaction present on its liquid phase, which would be more adequate to evaluate the methodologies under investigation, and this particular ionic liquid for the quality of the experimental data and its wide temperature range [23,28,32–35].

Fig. 1 shows that the density of this IL has a linear dependency on the temperature as previously described [23,28,32,33,35,36], and considering V_m constant maybe not suitable.

$$\rho\left(\text{kg m}^{-3}\right) = 1.4151 \times 10^3 - 0.7157T\,(\text{K}) \tag{12}$$

The viscosity experimental data [23,28,32,33,35,36] were fitted using the Ghatee, Litovitz and VFT equations (Fig. 1b, Table 1). The low RMSE values demonstrate a good accuracy of the three models to describe experimental data.

The expressions obtained by fitting the density and viscosity experimental data of [Bmim][BF$_4$] were used to estimate the activation parameters by the various methods. For Method 1, the polynomial parameters of Eq. (7) were 2.374×10^{-4}, -0.1930 and 34.199, for *a, b* and *c*, respectively. The RMSE was 0.0614, which represents a good description of the experimental data by the quadratic polynomial. However, the low value of coefficient *a* demonstrates that the plot $\ln\eta$ versus T approximates to a straight line, as shown in Fig. 2a, and it could be reduced to Method 2. In Method 1, viscous flow activation parameters, calculated from the polynomial parameters, depends on temperature. $\Delta G^{\ddagger}$ (Fig. 3a), obtained directly by the Eyring equation (Eq. (1)), presented a decreasing behavior. $\Delta G^{\ddagger}$ ranged from 27.82 to 26.41 kJ mol^{-1}, corresponding to an overall variation of only 1.41 kJ mol^{-1}. The upward concavity and the minima point close to 360 K has no physical meaning. Regarding $\Delta H^{\ddagger}$, Fig. 3(b), a considerable decrease is observed and the $\Delta H^{\ddagger}$ variation considering the whole temperature range was 28.30 kJ mol^{-1}. $\Delta S^{\ddagger}$ (Fig. 3c) showed similar behavior to $\Delta H^{\ddagger}$; though, there is an inversion in the entropy sign around 355 K, becoming negative for higher temperatures. The $\Delta C_P{}^{\ddagger}$ (Fig. 3d) presents a monotonous decreasing value.
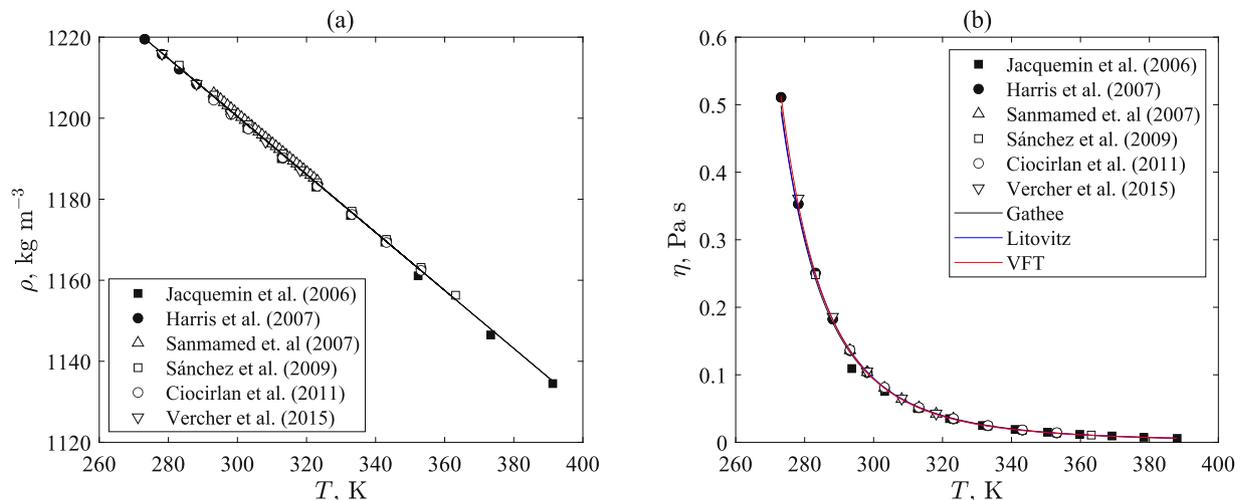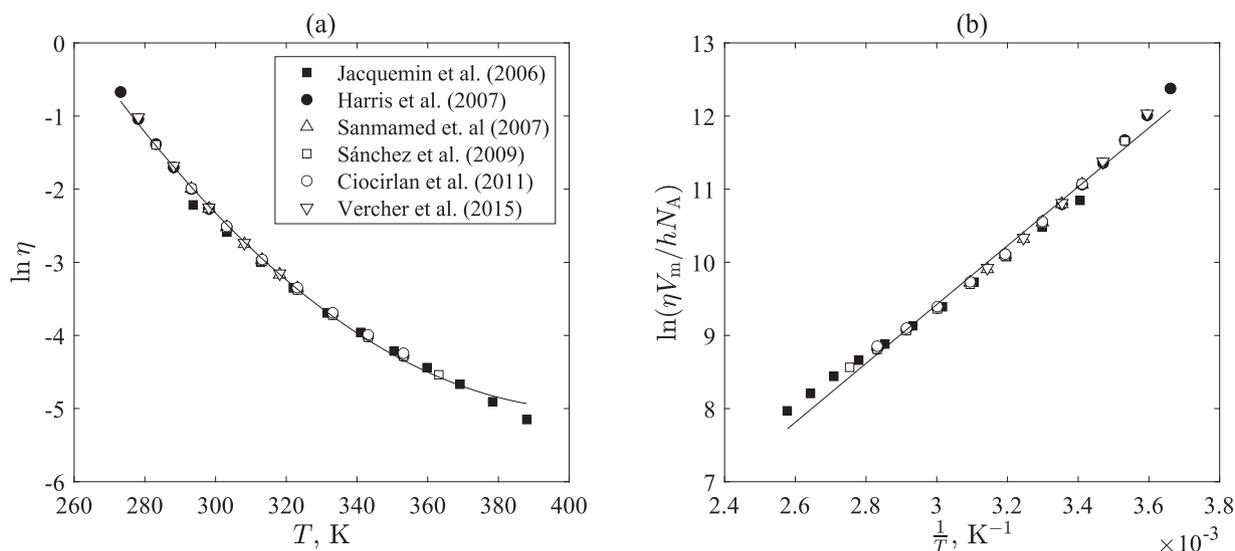

Fig. 1. Density (a) and viscosity (b) *vs.* temperature for [Bmim][BF$_4$]. The solid points belong to experimental data while the lines correspond to fitting.

Fig. 2. Viscosity experimental data of [Bmim][BF4]: (a) Method 1 (Eq. (7)), (b) Method 2 (Eq. (10)). The solid points belong to experimental data while the lines correspond to fitting.

Table 1
Fitted parameters for [BMIM][BF$_4$] viscosity experimental data to Litovitz, VFT, and Ghatee et al. equations.

| VFT				Litovitz			Gathee*		
A' (Pa s)	B' (K)	T_0 (K)	RMSE	A (Pa s)	B (R K^3)	RMSE	a' (Pa s)$^{-0.3}$ K^{-1}	b' (Pa s)$^{-0.3}$	RMSE
8.0978×10^{-5}	976.72	161.58	0.0032	6.1148×10^{-4}	1.1328×10^{9}	0.0350	0.0299	-6.9340	0.0230

* $\varphi = 0.3$, as suitable for several IL [25].

For Method 2, the linear adjust of the plot $\ln(\frac{\eta V_m}{h N_A})$ vs. $1/T$ (Eq. (10)) was performed, being the slope and the intercept 4.025×10^3 and -2.653, respectively. The RMSE was 0.1141, which represents a good description of the experimental data by a straight line. In this case, a physical interpretation may be attributed to those values according to Equation 14, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 33.47 kJ mol^{-1} and 0.0221 kJ K^{-1} mol^{-1}, respectively. $\Delta G^{\ddagger}$ be-

comes a linear function of temperature (Fig. 4), varying from 27.4 to 24.9 kJ mol^{-1}, and the overall variation range was 2.5 kJ mol^{-1}. Thus, considering only the determination of $\Delta G^{\ddagger}$, Methods 1 and 2 give very similar results, especially in narrow temperature ranges. Regarding $\Delta H^{\ddagger}$, besides the differences due to initial assumptions, they are in good agreement with similar values. For $\Delta S^{\ddagger}$, on the other hand, it was observed a difference in the sign of this
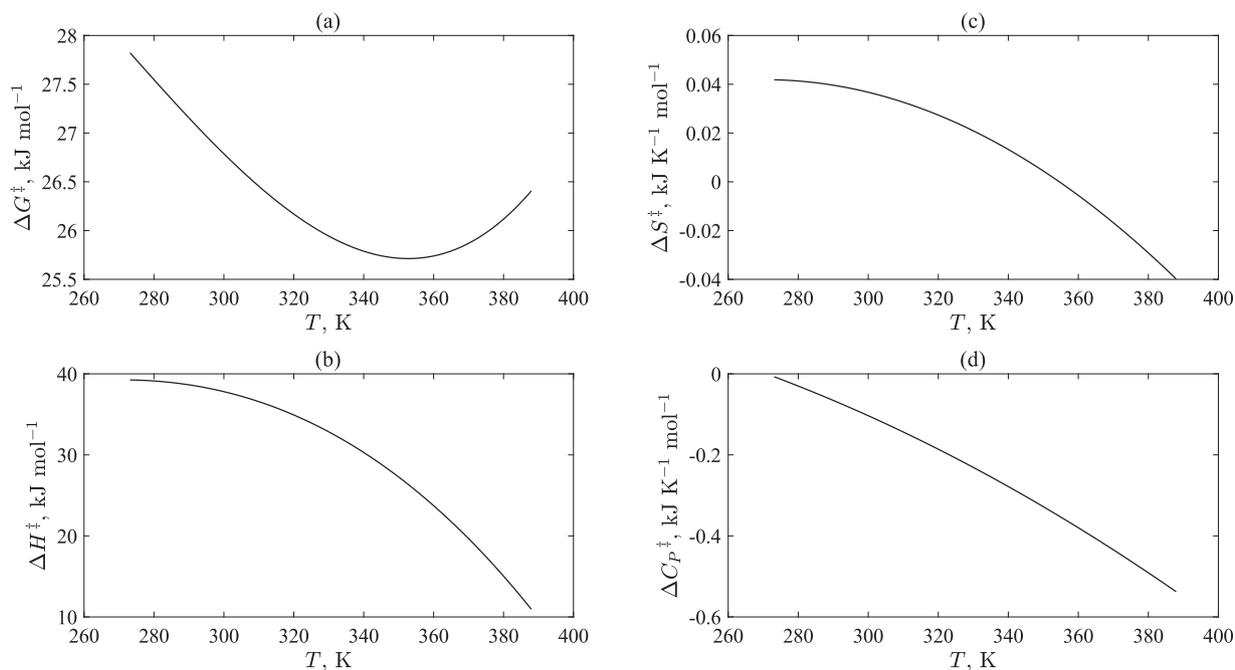
Fig. 3. Activation parameters of viscous flow *vs.* temperature for [Bmim][BF$_4$] obtained by Method 1. (a) $\Delta G^{\ddagger}$, (b) $\Delta H^{\ddagger}$, (c) $\Delta S^{\ddagger}$, (d) $\Delta C_P^{\ddagger}$.
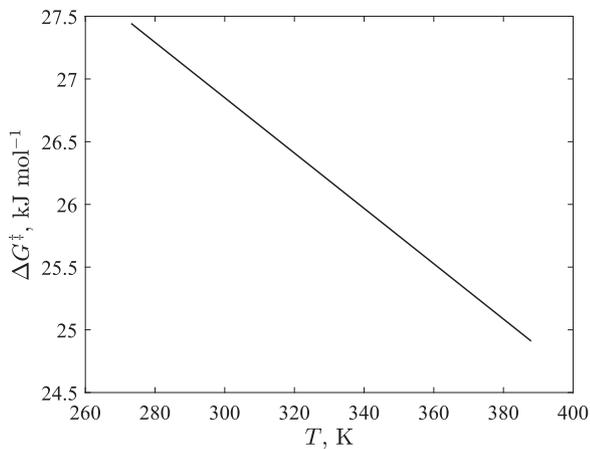
Fig. 4. Gibbs energy of activation of viscous flow *vs.* temperature of [Bmim][BF$_4$] obtained by Method 2. Other parameters are constant: $\Delta H^{\ddagger} = 33.47$ kJ mol^{-1}, $\Delta S^{\ddagger} = 0.0221$ kJ K^{-1} mol^{-1}, $\Delta C_P^{\ddagger} = 0$.

parameter what is very significant. Method 1 observes a sign inversion at about 380 K, while Method 2 considers entropy always positive, leading to an opposite physical interpretation of the phenomena involved, as hereafter discussed.

Method 3 is based on the viscosity being fitted by empirical models (Litovitz, VFT and Ghatee equations) and its derivative with respect to temperature (Fig. 5). This method does not consider any parameter ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ or V_{m}) constant, being applicable in wide ranges of temperature. $\Delta G^{\ddagger}$ presented similar behavior as obtained by Method 1, and the value decreased with temperature. The activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta C_P^{\ddagger}$ all decreased with temperature, and the chosen viscosity model did not influence the qualitative results. The $\Delta H^{\ddagger}$ variation considering the whole temperature range was about 10.66, 13.36 and 15.18 kJ mol^{-1} for Litovitz, VFT and Ghatee equations, respectively; lower values than those obtained by Method 1. The $\Delta S^{\ddagger}$ presented the same decreasing trend

Table 2
Summary of the trends of activation parameters of viscous flow of [Bmim][BF$_4$] obtained by Methods 1, 2 and 3.

Method	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta C_P^{\ddagger}$
1	Positive	Positive	Positive (mostly)	Sign inversion
	Decreasing	Decreasing	Decreasing	Decreasing
2	Positive	Positive	Positive	zero
	Decreasing	Constant	Constant	Constant
3	Positive	Positive	Positive	Negative
	Decreasing	Decreasing	Decreasing	Increasing

as $\Delta H^{\ddagger}$ (Fig. 5c) while $\Delta C_P^{\ddagger}$ was negative and increased with temperature. Those results were reproducible for each viscosity data set evaluated separately (Figs. 6 to 8).

Table 2 summarizes the dependency of the viscous flow activation parameters obtained for [Bmim][BF$_4$] by the three methods. $\Delta G^{\ddagger}$ showed the same trend and order of magnitude in all three methods, what is expected as this parameter is obtained directly from the Eyring equation. The decreasing values of Gibbs free energy indicate that less energy is necessary to start the viscous flows [14], i.e., the viscosity of IL decreases with temperature, a consequence of the weakening of molecular interactions in the fluid [21]. The $\Delta H^{\ddagger}$ were positive for three calculation methods and showed the same order of magnitude, about 26 kJ mol^{-1}. Positive and large values for $\Delta H^{\ddagger}$ may be due to the substantial degree of order leading to cooperative movement entities, characteristic of highly structured liquids [1]. However, in what concerns the temperature dependency, considerable differences were observed. The function obtained by Method 1 presented a downward concavity, i.e., both the $\Delta H^{\ddagger}$ and its change rate are decreasing. For Method 2, $\Delta H^{\ddagger}$ is constant. For Method 3, the upward concavity means that the function is decreasing, but the variation rate increases with temperature − the differences in the shape of $\Delta H^{\ddagger}$ influences the interpretation of its derivative, $\Delta C_P^{\ddagger}$, as further detailed below.

The most relevant differences in the activation parameters were observed on $\Delta S^{\ddagger}$ and $\Delta C_P^{\ddagger}$, that depending on the calculation method, may present positive or negative values. The $\Delta S^{\ddagger}$
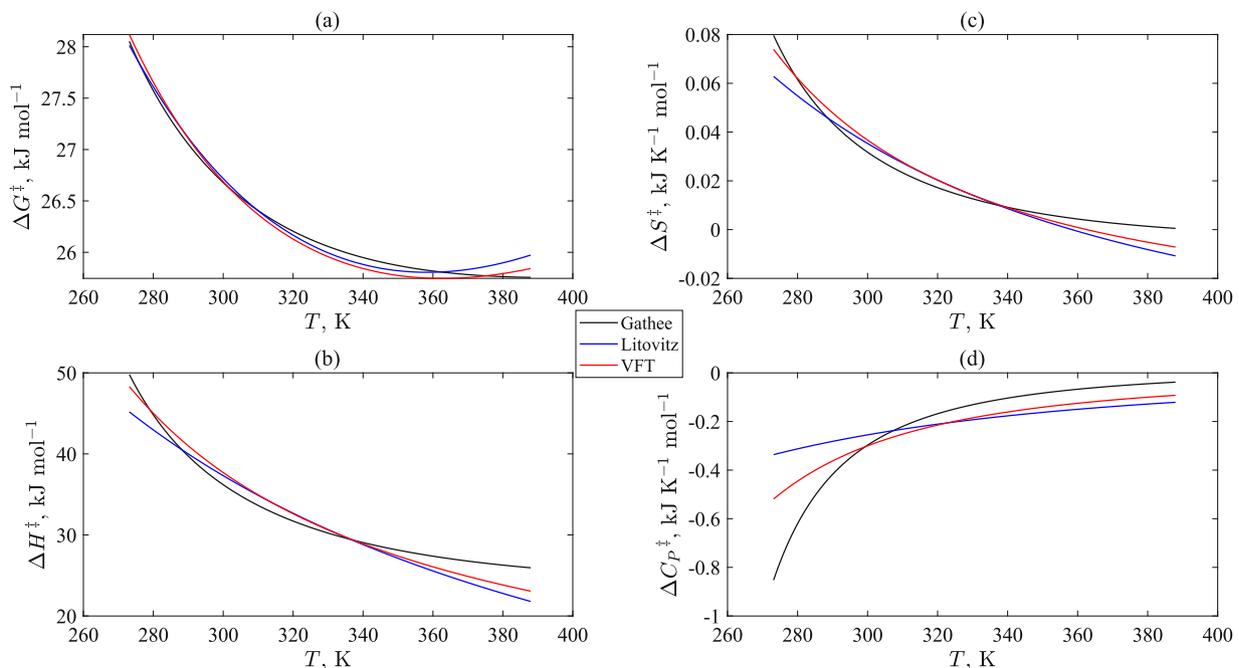
Fig. 5. Activation parameters of viscous flow *vs.* temperature of [Bmim][BF$_4$] obtained by Method 3 and three empirical models for viscosity data. (a) $\Delta G^{\ddagger}$, (b) $\Delta H^{\ddagger}$, (c) $\Delta S^{\ddagger}$, (d) $\Delta C_P^{\ddagger}$.
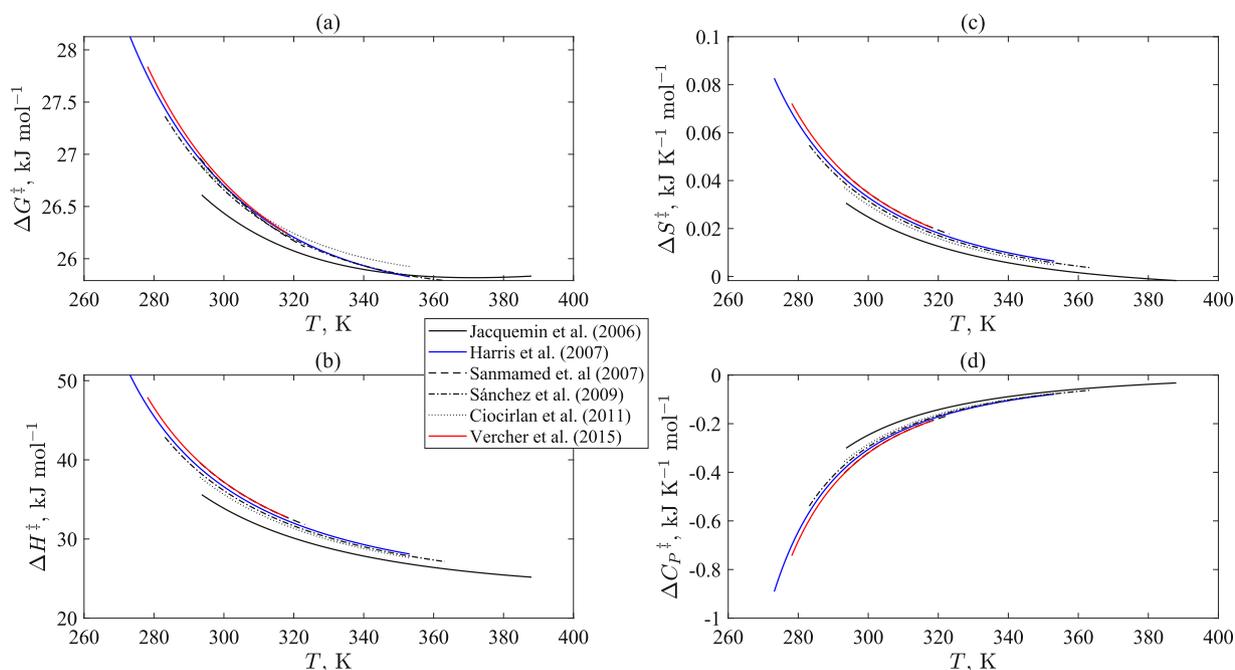
Fig. 6. Comparison of Activation parameters of viscous flow *vs.* temperature for [Bmim][BF$_4$] obtained by Method 3 and Ghatee equation. (a) $\Delta G^{\ddagger}$, (b) $\Delta H^{\ddagger}$, (c) $\Delta S^{\ddagger}$, (d) $\Delta C_P^{\ddagger}$.
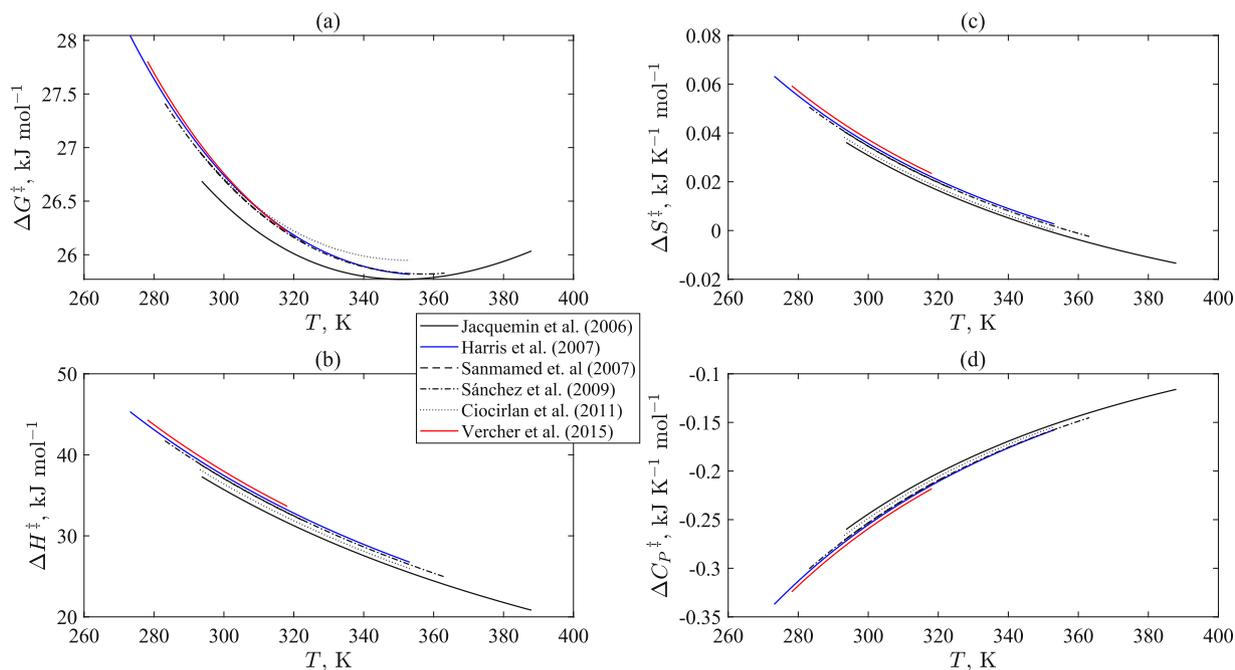

Fig. 7. Comparison of Activation parameters of viscous flow *vs.* temperature for [Bmim][BF$_4$] obtained by Method 3 and Litovitz equation. (a) $\Delta G^{\ddagger}$, (b) $\Delta H^{\ddagger}$, (c) $\Delta S^{\ddagger}$, (d) $\Delta C_P^{\ddagger}$.

temperature dependency was similarly to $\Delta H^{\ddagger}$; however, the difference in sign leads to opposite interpretations of molecular interactions. Positive values of entropy mean an increase of the system disorganization during viscous flow, due to the disruption of molecular interactions by the action of shear forces [37]. In contrast, negative values are related to the development of a more structured fluid during viscous flow and the formation of an activation complex [1]. Method 1 suggests that at high temperatures (above 370 K), the fluids become more structured during viscous flow, which is a characteristic of rheological transitions of non-

Newtonian fluids [38]. However, the Newtonian behavior of ionic liquids in general, and [Bmim][BF$_4$] in particular, is not coherent with these results [23,39]. The estimated $\Delta S^{\ddagger}$ is positive, as expected, for both methods 2 and 3, presenting either a constant or decreasing value, respectively.

Finally, the $\Delta C_P^{\ddagger}$ was addressed. This parameter is widely studied for mechanistic studies transition states of chemical reactions. In this case, it is related to the extension of the solvent reorganization during the activation process [40–43]. According to these studies, negative values of $\Delta C_P^{\ddagger}$ are attributed to a stabilization of
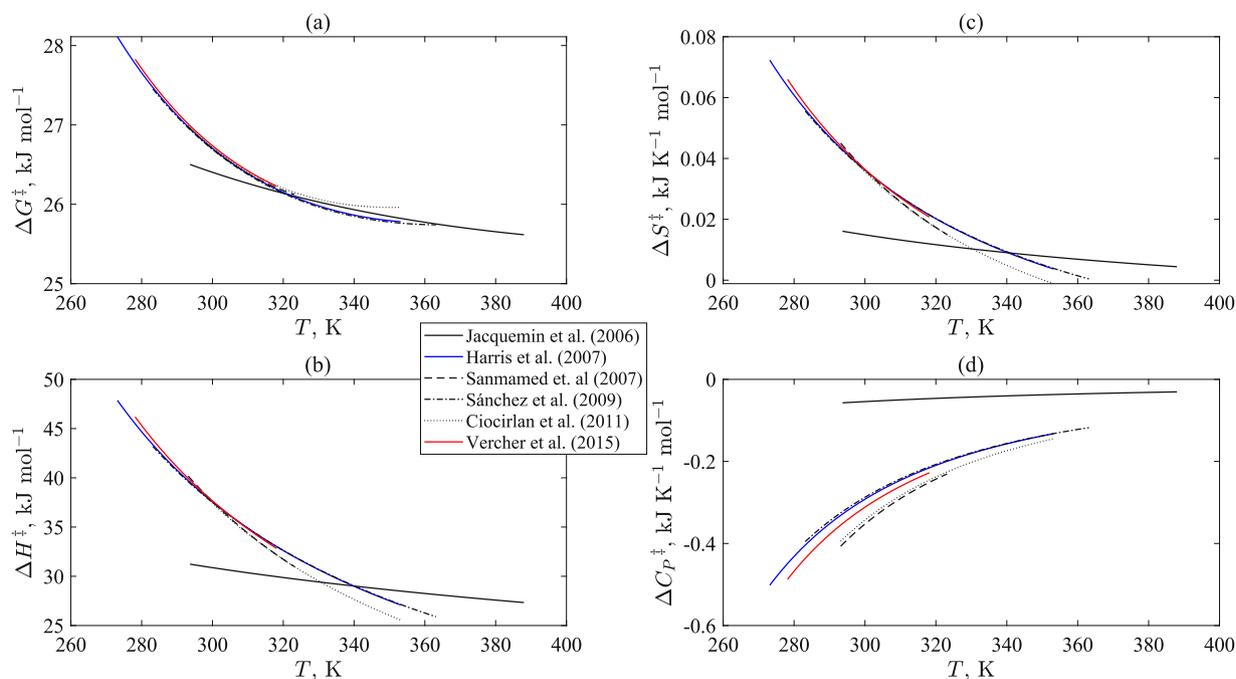
Fig. 8. Comparison of Activation parameters of viscous flow *vs.* temperature for [Bmim][BF$_4$] obtained by Method 3 and VFT equation. (a) $\Delta G^{\ddagger}$, (b) $\Delta H^{\ddagger}$, (c) $\Delta S^{\ddagger}$, (d) $\Delta C_P{}^{\ddagger}$.

the transition state of a chemical reaction, while positive values to a disruption of the activated state. Analogously, $\Delta C_P{}^{\ddagger}$ of viscous flow is related to the transition state necessary for starting the flow. Negative values are related to the stabilization of the transition state, while positive values are correlated to its disruption during the viscous flow. Again, the sign inversion observed in the parameter values estimated by Method 1 represents a change in the viscosity behavior that it is not supported by the Newtonian behavior of [Bmim][BF$_4$] [39,44]. The $\Delta C_P{}^{\ddagger}$ equals zero for Method 2 and was predominantly negative for Method 3, which means either no formation of transition state or its stabilization during viscous flow. Besides the extensive calculation of this parameter for viscosity data, the physical interpretation of this parameter has been, so far, poorly explored in the literature for systems containing ILs.

The results of the activation parameters based in Method 1, can lead to a misinterpretation of the thermodynamic behavior and should be avoided. Method 2 provides limited information; since it does not evaluate the effect of temperature on $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta C_P{}^{\ddagger}$ functions; though, it is advantageous to evaluate the variation of these parameters with the composition in binary mixtures, as widely accepted and reported. This evaluation shows that the Method 3 is the most appropriate for the estimation of the activation parameters of the viscous flow of pure substance in broad temperature ranges. This methodology provides the most reliable interpretation, achieved through a still simple mathematical calculation.

3.2. Study of activation parameters of viscous flow for pure compounds

To better assess the ability of Method 3 to estimate viscous activation parameters, calculations were performed for several substances. Two classes of compounds were here chosen: alkanes (C5 to C12), due to simple nature of their intermolecular interactions, the availability of their physical properties, and their relevance in the chemical industry [3]; and ionic liquids, due to emerging possibilities of their use (solvents, catalysts, lubricants) [19,21], the complexity of their intermolecular interactions, and abnormal physical properties [45].

3.3. Alkanes

Fig. 9 shows the activation parameters of the viscous flow for alkanes. The experimental data were obtained from the NIST databank [46]. For the lower alkanes (pentane, hexane, and heptane), it is possible to observe a considerable variation of the activation parameters at higher temperatures, as they approach the critical point (Table 3). The $\Delta G^{\ddagger}$ increased with both temperature and carbon number. Its variation between pentane and dodecane at 270 K was 6 kJ mol^{-1}. This was previously reported [47–49] and it was attributed to a considerable degree of order of low weight *n*-alkanes. At low temperatures, *n*-alkanes are present in a *quasi*-crystalline state, i.e., where the intermolecular space ranges are just slightly higher than solid crystalline state [47]. At high temperatures, *n*-alkanes gain a rotational degree of freedom, as they can rotate along their molecule long axis.

The $\Delta H^{\ddagger}$ were positive for all alkanes and their behavior may be classified according to the carbon number. Pentane, hexane and heptane presented a similar behavior, where $\Delta H^{\ddagger}$ increase until temperatures become closer to critical points. Octane and nonane correspond to a boundary in the behavior inversion. While for octane, the $\Delta H^{\ddagger}$ still increases, for nonane, it decreases. For decane, undecane and dodecane, the $\Delta H^{\ddagger}$ presents a similar behavior: a minimum at 370, 380 and 390 K, respectively. The enthalpy activation for a viscous flow is a measure of the degree of cooperation between species taking part in the viscous flow [1]: in structured fluids, the movement of dislocation requires at least two moving molecules, one moving out and one moving into a regular lattice position [47,50]. According to Moore et al. [47], the enthalpy minima correspond to the "transition point" separating the high structured fluids at low temperatures and lower structured fluids at higher temperatures, in which molecules can rotate along their major axis.

The $\Delta S^{\ddagger}$ were negative for the whole temperature range, presenting a temperature dependency that varies with the chain length. For the lower alkanes, the entropy increases with temperatures, i.e., the fluids tend to be less ordinate. For alkanes with more than 8 carbons, it is possible to observe a minimum attributed to the previously mentioned "transition point". Lastly,
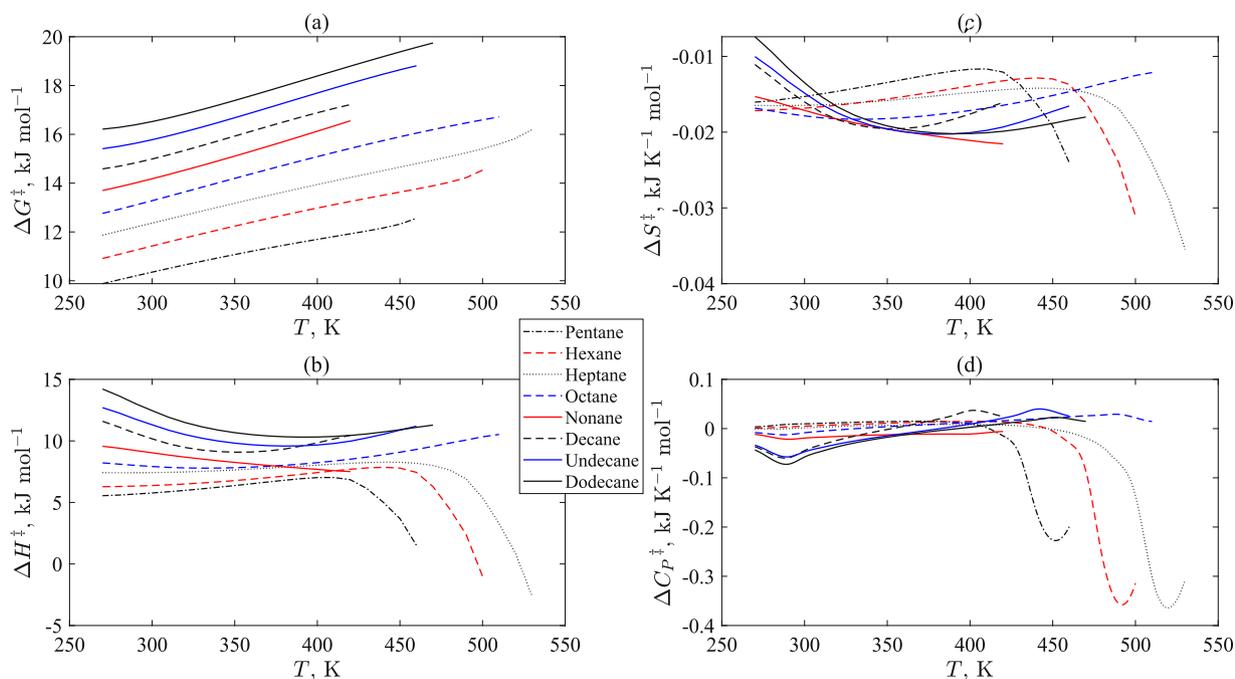
Fig. 9. Activation parameters for viscous flow *vs.* temperature for alkanes containing for 5 to 12 carbons: (a) $\Delta G^{\ddagger}$, (b) $\Delta H^{\ddagger}$, (c) $\Delta S^{\ddagger}$, (d) $\Delta C_P{}^{\ddagger}$.

Table 3
Critical and phase transition properties of alkanes containing 5 to 12 carbons: compressibility factor (Z_c), molar volume (V_c), pressure P_c, temperature T_c, boiling temperature T_b and melting temperature T_f. [46].

Compound	Z_c	V_c, m³ mol⁻¹	P_c, MPa	T_c, K	T_b, K	T_f, K
Pentane	0.2691	0.00031	3.36729	469.73	309.21	143.48
Hexane	0.2654	0.00037	3.02760	507.55	341.861	177.88
Heptane	0.2609	0.00043	2.73490	540.08	371.53	182.60
Octane	0.2584	0.00049	2.48670	568.78	398.783	216.42
Nonane	0.2597	0.00056	2.29295	594.13	423.79	219.68
Decane	0.2531	0.00062	2.11439	618.05	447.27	243.54
Undecane	0.2477	0.00066	1.99307	638.81	469.057	247.61
Dodecane	0.2504	0.00076	1.81152	658.24	489.45	263.60

for $\Delta C_P{}^{\ddagger}$, negative values were observed, with larger modules at lower temperatures. However, there is a change in this tendency for lighter molecules at elevated temperatures, for which comparatively higher negative values of $\Delta C_P{}^{\ddagger}$ being observed. This result has to do with the behavior observed for $\Delta H^{\ddagger}$ and discussed earlier. Thus, the difference of energy between transition state for viscous flow and steady fluid is more pronounced for the heavier alkanes. The behavior and the order of magnitude of all three parameters agreed with those previously reported for alkanes with 6 to 20 carbons at 313.15 K, 343.15 K and 383.15 K [49]. Positive enthalpy and negative entropy are ascribed to simple substances as alkanes [47].

3.4. Ionic liquids

Fig. 10 shows the activation parameters for viscous flow obtained from reported experimental data [25] for selected aprotic ionic liquids (AIL). $\Delta G^{\ddagger}$ is almost constant in the studied temperature range for all AILs. The magnitude of $\Delta G^{\ddagger}$ decreases as follows, [Bmim][PF$_6$]> [N$_{4111}$][NTf$_2$]> [Emim][EtSO$_4$]> [Bmim][BF$_4$] > [Bmim][NTf$_2$]> [Emim][NTf$_2$], the same order of IL hydrogen-bonds basicity decrease [22,51]. IL basicity is related to a strong coordination ability [22], and thus have a positive correlation with the energy necessary to develop the viscous flow.

Positive and high values for $\Delta H^{\ddagger}$ indicates the occurrence of co-operative movement confirming the highly structured nature of IL [1]. $\Delta S^{\ddagger}$ were positive for all studied AIL, except for [Emim][EtSO$_4$]. Positive values for entropy are related to a decrease in fluid organization due to intermolecular disruption. The negative value for [Emim][EtSO$_4$] suggests the formation of an activation process. $\Delta C_P{}^{\ddagger}$ approximates to zero at higher temperatures, showing a lower difference in energy of transition state for viscous flow at higher temperatures, as previously discussed.

Fig. 11 shows the results for activation parameters of viscous flow using reported experimental data [2] for selected protic ionic liquids (PIL): 2-HDEAA, 2-HEAPr, 2-HDEAL, 2-HEAL and 2-HEAA. Excepting for $\Delta G^{\ddagger}$, the results were significantly different from those calculated using Method 1 reported by Camargo et al. [2]. According to Method 3, the $\Delta H^{\ddagger}$ were positive for all PIL, which is coherent with the high organization of those compounds in the liquid phase. $\Delta S^{\ddagger}$ positive values are related to a decrease in the system organization during viscous flow, and thus, no activation complex formation as in AIL. $\Delta C_P{}^{\ddagger}$ was negative and increased with temperature due to a lower difference in the energy of transition for viscous flow. Camargo et al. [2] reported negative values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, as well as constant $\Delta C_P{}^{\ddagger}$. $\Delta H^{\ddagger}$ negative values suggest that these PILs have a non-shear-thickening structure [12], which is not in agreement with the observed Newtonian behavior
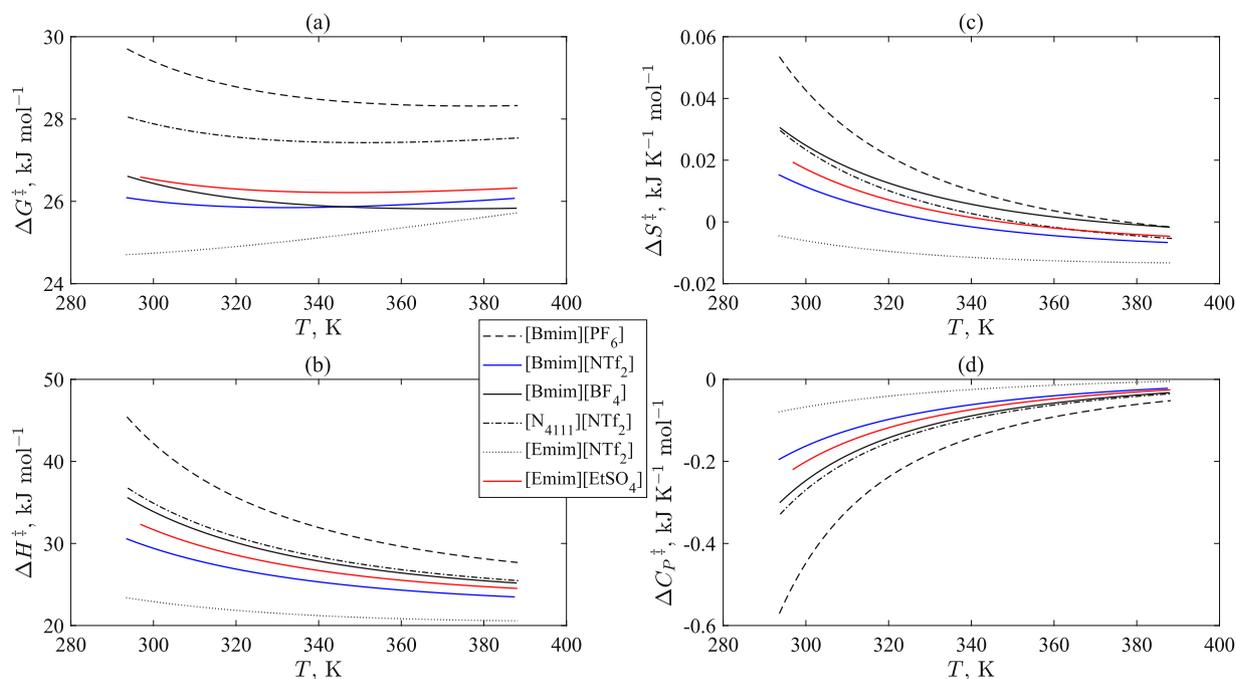
Fig. 10. Activation parameters of viscous flow *vs* temperature for selected AILs obtained by Method 3 and Ghatee equation. (a) $\Delta G^\ddagger$, (b) $\Delta H^\ddagger$, (c) $\Delta S^\ddagger$, (d) $\Delta C_P^\ddagger$.
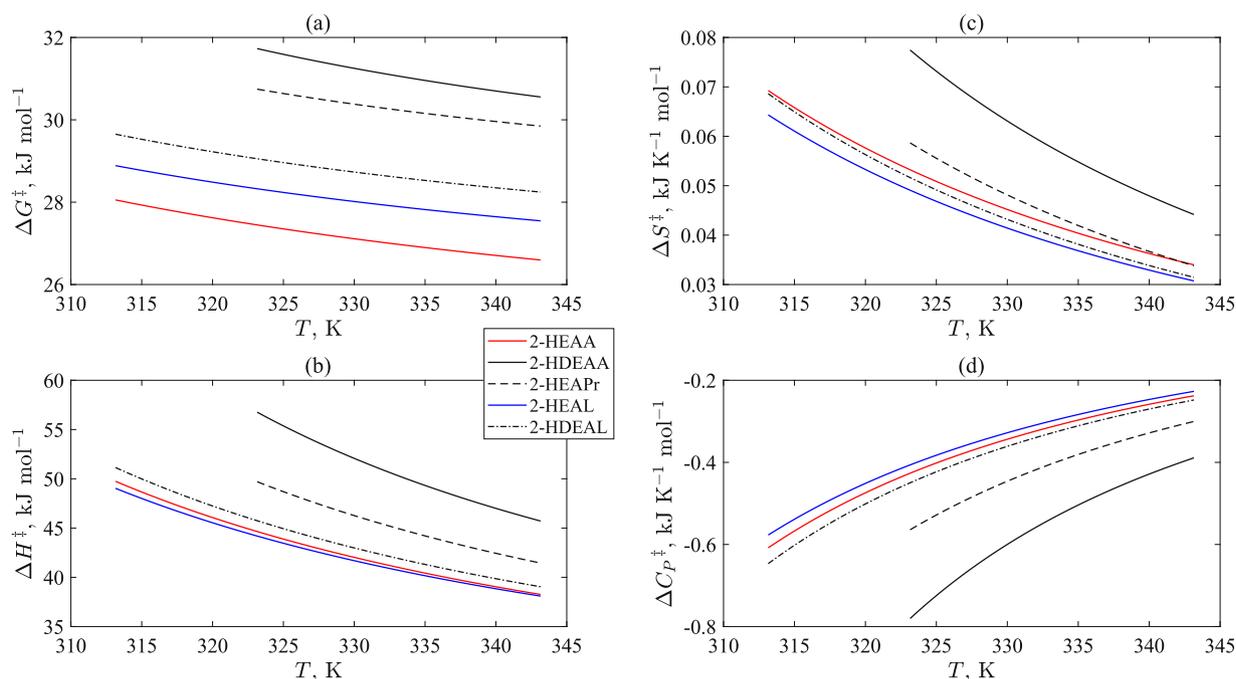

Fig. 11. Activation parameters of viscous flow *vs.* temperature for selected PILs obtained by Method 3 and Ghatee equation. (a) $\Delta G^\ddagger$, (b) $\Delta H^\ddagger$, (c) $\Delta S^\ddagger$, (d) $\Delta C_P^\ddagger$.

of those compounds. Positive enthalpy along with positive $\Delta S^\ddagger$ are attributes of complex substances [47], and thus in good agreement with what can be expected from protic ionic liquids.

4. Conclusion

This work evaluated two different methodologies for calculating the viscous activation parameters for the ionic liquid [Bmim][BF$_4$], here so-called Method 1 and 2, that were proved unsatisfactory. Method 1 considers that the molar volume of the substances is constant with the temperature. The development based only on the mathematical nature of the experimental data resulted in vis-

cous activation parameters without physical meaning, or leading to incorrect interpretations about the nature of the liquid phase. Method 2 considers that enthalpies and entropies of activation are constant with temperature and a function of composition, which is useful for the study of binary mixtures, but oversimplifies the analysis for pure compounds. Then, a methodology here so-called Method 3, first proposed in this work, considers all parameters a function of temperature through simple mathematical models. The application of Method 3 for the calculation of the activation parameters of alkanes and ionic liquids confirmed the estimations of parameters consistent with the interpretation of the physical phenomena observed in the viscous flow. Fewer restrictions in the

development of calculations by this last approach allows it to be applied in wider temperature ranges.

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.

CRediT authorship contribution statement

Lucas J. dos Santos: Methodology, Software, Formal analysis. **Luis Alonso Espinoza-Velasquez:** Conceptualization. **João A.P. Coutinho:** Supervision. **Simone Monteiro:** Visualization, Funding acquisition, Project administration, Writing - review & editing.

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