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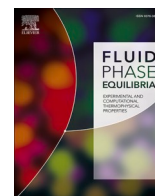
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Coupling cubic equations of state with the concept of entropy scaling to model the viscosity of ionic liquids

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ABSTRACT

This short paper investigates the applicability of our previously developed entropy scaling model to pure ionic liquids and concludes that it can be used without any modification and leads to very satisfactory results when coupled with the Peng-Robinson or Soave-Redlich-Kwong cubic equations of state. For the considered ionic liquids, the average deviations between calculated and experimental viscosities were found to be around 4.6 and 5.8% for the two cubic equations of state, respectively.

1. Introduction

With their tunable physicochemical properties [1], application fields of ionic liquids span over a wide range of disciplines. Viscosity is a critical parameter and its characterization is of major importance for electrochemical [2], lubrication and separation [3] and renewable energy [4,5] processes. Diverse physical, semi-empirical and empirical models were developed in the last years to give reliable predictions of the viscosity of ionic liquids (ILs) [6]. Among them, the friction theory [7–11], the free volume theory [7–9,12,13] have been successfully applied to correlate viscosity of some ionic liquids. Based on Eyring's theory, Macias-Salinas proposed a model that also proved to be a promising approach [14]. More recently, the entropy scaling concept which correlates the viscosity to the residual entropy was investigated by Macias-Salinas and Gross [15] for its applicability to ionic liquids. The aforementioned methods count among the most physically-sound approaches in modeling viscosities of fluids; their optimal formulation is still an open question as multiple versions of such models – with different numbers of adjustable parameters – can be found in the literature.

In this note, following the recent study of Macias-Salinas and Gross [15], the applicability of a reformulated entropy scaling model, previously developed by our group [16–22], is investigated. The same ionic liquids as those selected by Macias-Salinas and Gross are here considered to investigate the performances of coupling the Peng-Robinson (PR) or Soave-Redlich-Kwong (SRK) equations of state with our version of the

entropy scaling concept.

2. Theoretical background

2.1. Entropy scaling

First proposed by Rosenfeld [23,24], the correlation of a reduced transport property in general and a reduced viscosity in particular with the T_v -residual entropy (i.e., the difference between the entropy of a real fluid and the entropy of a perfect gas having the same temperature and volume as the real fluid) has given good results and proved robustness for a wide range of fluids and temperature and pressure conditions. By reduced transport properties, we mean that the actual transport property is divided by a reference term of the same dimension. In Rosenfeld's original publication, the entropy scaling concept is justified by the fact that the transport properties of some simple theoretical fluids (hard spheres) can be expressed as functions of the packing fraction which in turn has a direct relation with the residual entropy. Beyond the specific case of model fluids, Dyre [25] summarizes the concept as follows: "The simplest explanation of excess-entropy scaling is that the microscopic dynamics at state points with the same excess entropy is virtually the same".

It thus becomes possible to derive a direct relationship between transport properties and residual entropy. The estimation of the residual entropy knowing the temperature and pressure conditions of a fluid can be made straightforwardly from an equation of state. Several improve-

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ments were achieved since the first appearance of the method in 1977. Through our investigations on viscosity [16], thermal conductivity [17] and diffusion coefficients [18] of a large panel of pure fluids, we have developed a reformulated version of the entropy scaling concept to achieve a better universality and a broad applicability while counteracting the systematic low-density divergence of the original approach [19]. The following thermodynamic function was used for the correlation of transport properties:

$$X_{ES} = \left(-\frac{s_{TV-res}}{s_{TV-res}^c} \right) - \ln \left(\frac{s_{TV-res}}{s_{TV-res}^c} \right) \quad (1)$$

s_{TV-res} is the Tv-residual entropy and s_{TV-res}^c is the corresponding critical value. The viscosity is then calculated as *the reference term* multiplied by a function ($e^{Y_{ES}}$) depending on the Tv-residual entropy, X_{ES} and parameters specific to each component:

$$\eta_{calc} = \eta_{ref} \cdot e^{Y_{ES}} \quad (2)$$

Here, the reference viscosity term is kept within its macroscopic form as proposed by Rosenfeld [23] and justified later by Dyre under the scope of the isomorph theory [25]:

$$\eta_{ref} = \rho_N^{2/3} \sqrt{m_0 k_b T} \quad (3)$$

Where ρ_N is the molecular density, m_0 the molecular mass in kg, k_b the Boltzmann constant and T the temperature. In Eq. (4), the logarithm of the reduced viscosity, Y_{ES} , is defined as a combination of dense fluid and gas contributions.

$$\left\{ \begin{array}{l} Y_{ES} = \ln \left(\frac{\eta}{\eta_{ref}} \right) = \left[f_{dense}(\tilde{s}_{TV-res}, a_1, a_2) \times g_{dense}(X_{ES}, c) + f_{gas}(\tilde{s}_{TV-res}, b_1, b_2) \times g_{gas}(X_{ES}, c) \right] \cdot X_{ES} + k \left(\frac{s_{TV-res}^c}{s_{TV-res}} \right), d \\ a_1, a_2, b_1, b_2, c \text{ and } d \text{ are component-dependent model parameters} \\ \tilde{s}_{TV-res} = \frac{s_{TV-res}}{R} \\ \text{When the model parameters are known, } \eta \text{ is the calculated viscosity } (\eta = \eta_{calc}) \\ \text{When the model parameters are fitted, } \eta \text{ is the experimental viscosity } (\eta = \eta_{exp}) \end{array} \right. \quad (4)$$

Where f_{dense} and f_{gas} are functions describing the dense-state behavior ($X_{ES} < 0$) and gas-state behavior ($X_{ES} > 0$) respectively; g_{dense} and g_{gas} can be considered as damping factors making f_{dense} dominating in the dense region, and conversely, f_{gas} dominating in the gas region. The definition of these functions is given in equations (5).

$$\left\{ \begin{array}{l} f_{dense}(\tilde{s}_{TV-res}) = a_1 + a_2 \cdot \tilde{s}_{TV-res} \\ g_{dense}(X_{ES}) = \frac{1}{1 + e^{cX_{ES}}} \\ f_{gas}(\tilde{s}_{TV-res}) = b_1 + b_2 \cdot \tilde{s}_{TV-res} \\ g_{gas}(X_{ES}) = \frac{1}{1 + e^{-cX_{ES}}} \\ k = \frac{d}{s_{TV-res}^c} \end{array} \right. \quad (5)$$

For a given fluid, the later correlating function introduces six parameters (a_1, a_2, b_1, b_2, c , and d) for the entire fluid region; they must be fitted to experimental data. The case of ionic liquids can be considered as a special case because, due to their very low vapor pressures, these compounds are, in practice, never gaseous. As the experimental viscosity data always refer to the liquid state, the approach presented above can be simplified by reducing Eq. (4) to the liquid part by setting the

parameters b_1, b_2 and c to zero: it is recalled that b_1 and b_2 are parameters involved in the expression of f_{gas} while c is a parameter of the damping factors g_{dense} and g_{gas} , used to bridge the dense fluid part and the gas part of the correlation Y_{ES} versus \tilde{s}_{TV-res} . Eq. (4) thus becomes:

$$Y_{ES} = \left[f_{dense}(\tilde{s}_{TV-res}) \times \frac{1}{2} \right] \cdot X_{ES} + k \quad (6)$$

Therefore, for a given ionic liquid, the correlation of the viscosity only requires the fitting of 3 parameters (a_1, a_2 and d).

2.2. Equations of state and experimental data

For the estimation of the thermodynamic properties, namely, the density and the Tv-residual entropy, involved in the model previously presented, translated versions [26–28] of the Peng-Robinson [29] and Soave-Redlich-Kwong [30] equations of state were used. The volume translation c_t , was estimated for each EoS and for each component using the correlations developed by Pina-Martinez et al. [31]. These correlations do not require new input parameters and are therefore not very accurate. However, they can be used to improve the liquid densities returned by the two cubic EoS (in particular the SRK EoS). As we shall see later, the main source of error with ILs is ignorance of the critical parameters and acentric factor. Although not consistent [32–34], a Soave-type temperature-dependent α -function was used in both EoS [35]. This is simply because using a consistent version of the Twu 91 α -function [36] would require vapor pressure data to determine the three parameters L, M and N embedded in such an α -function, whereas

such data are not available for ionic liquids.

t-PR:

$$P(T, v) = \frac{RT}{(v + c_t) - b} - \frac{a(T)}{(v + c_t)(v + c_t + b) + b(v + c_t - b)} \quad (7)$$

$$\text{With : } \left\{ \begin{array}{l} \eta_c = \left[1 + \sqrt[3]{4 - 2\sqrt{2}} + \sqrt[3]{4 + 2\sqrt{2}} \right]^{-1} \approx 0.25308 \\ a_c = \frac{40\eta_c + 8}{49 - 37\eta_c} \frac{R^2 T_c^2}{P_c} \approx 0.45724 \frac{R^2 T_c^2}{P_c} \\ b = \frac{\eta_c}{\eta_c + 3} \frac{RT_c}{P_c} \approx 0.07780 \frac{RT_c}{P_c} \\ c_t = \frac{RT_c}{P_c} (0.0096 + 0.0048\omega) \\ a(T) = a_c \cdot \alpha(T_r); T_r = \frac{T}{T_c} \\ \alpha(T_r, \omega) = [1 + m(\omega)(1 - T_r^{0.5})]^2 \\ m = 0.3919 + 1.4996\omega - 0.2721\omega^2 + 0.1063\omega^3 \end{array} \right. \quad (8)$$

t-SRK:

$$P(T, v) = \frac{RT}{(v + c_t) - b} - \frac{a(T)}{(v + c_t)(v + c_t + b)} \quad (9)$$

Table 1
Critical properties and acentric factor of the considered ionic liquids.

Ionic liquid	M, g/mol	T _c , K	P _c , bar	ω	Source
[emim][BF ₄]	198.0	585.3	23.6	0.7685	[37]
[bmim][BF ₄]	226.0	632.3	20.4	0.8489	[37]
[hmim][BF ₄]	254.1	679.1	17.9	0.9258	[37]
[omim][BF ₄]	282.1	726.1	16.0	0.9954	[37]
[bmim][PF ₆]	284.2	708.9	17.3	0.7553	[37]
[hmim][PF ₆]	312.2	754.3	15.5	0.8352	[37]
[omim][PF ₆]	340.3	800.1	14.0	0.9069	[37]
[emim][TF ₂ N]	391.3	1244.9	32.6	0.1818	[37]
[bmim][TF ₂ N]	419.4	1265.0	27.6	0.2656	[37]
[hmim][TF ₂ N]	447.4	1287.3	23.9	0.3539	[37]
[b3mpy][BF ₄]	237.0	625.8	18.9	0.8924	[39]
[P14][TF ₂ N]	422.4	1093.1	24.25	0.3467	[39]
[N1114][TF ₂ N]	396.4	1038.7	25.9	0.3334	[38]

$$\text{With : } \begin{cases} a_c = \frac{1}{9(\sqrt[3]{2}-1)} \frac{R^2 T_c^2}{P_c} \approx 0.42748 \frac{R^2 T_c^2}{P_c} \\ b = \frac{\sqrt[3]{2}-1}{3} \frac{R T_c}{P_c} \approx 0.08664 \frac{R T_c}{P_c} \\ c_t = \frac{R T_c}{P_c} (0.0227 + 0.0093\omega) \\ \alpha(T) = a_c \cdot \alpha(T_r); T_r = \frac{T}{T_c} \\ \alpha(T_r, \omega) = [1 + m(\omega)(1 - T_r^{0.5})]^2 \\ m = 0.4810 + 1.5963\omega - 0.2963\omega^2 + 0.1223\omega^3 \end{cases} \quad (10)$$

Each of the two equations of state takes the critical temperature, critical pressure and the acentric factor as input parameters. For ILs, these parameters can not be determined experimentally and are

Table 2
Experimental viscosity data base of pure ionic liquids.

Ionic liquid	number of exp. data points	T _{min} /K	T _{max} /K	P _{min} /bar	P _{max} /bar	η _{min} /(mPa.s)	η _{max} /(Pa.s)	Source
[emim][BF ₄]	54	282.55	323.75	1	145	18.4	0.0793	[40]
[bmim][BF ₄]	108	273.15	353.15	1	3000	13.2	0.875	[41,42]
[hmim][BF ₄]	53	293.15	353.15	1	1218.1	21.2	0.819	[43,44]
[omim][BF ₄]	101	273.15	353.15	1	2242	28.1	2.291	[44,45]
[bmim][PF ₆]	93	273.15	353.15	1	2493	25.5	2.694	[41,46]
[hmim][PF ₆]	108	273.15	353.15	1	2385	34.7	3.924	[43,47,48]
[omim][PF ₆]	76	273.15	353.15	1	1759	42.2	6.41	[45,47]
[emim][TF ₂ N]	87	298.15	353.15	1	1255.3	7.81	0.1315	[43,49]
[bmim][TF ₂ N]	119	273.15	353.15	1	2989	9.50	0.2803	[48,49]
[hmim][TF ₂ N]	115	288.15	433.15	1	1240	2.86	0.2757	[43,50]
[b3mpy][BF ₄]	69	278.15	333.15	0.7	650.5	30.5	1.281	[51,52]
[P14][TF ₂ N]	91	273.15	353.15	1	1029.2	12.7	1.18476	[53]
[N1114][TF ₂ N]	76	278.15	373.15	0.991	1500	9.36	0.5666	[54]

Table 3
Model's adjusted parameters for the t-PR EoS and the corresponding average deviations.

CAS number	IL name	a ₁	a ₂	d	Number of exp. data points	MAPE%
143314-16-3	[emim][BF ₄]	9.48657086	0.50377187	-39.4435442	54	1.30
174501-65-6	[bmim][BF ₄]	9.42749657	0.4810409	-40.179586	108	5.91
244193-50-8	[hmim][BF ₄]	14.4133333	0.58419788	-69.9247529	53	5.82
244193-52-0	[omim][BF ₄]	9.57222427	0.38666072	-50.0100974	101	4.43
174501-64-5	[bmim][PF ₆]	14.6227305	0.68109464	-61.9788771	93	7.05
304680-35-1	[hmim][PF ₆]	14.8960178	0.61449464	-70.2641308	108	6.55
304680-36-2	[omim][PF ₆]	12.7538506	0.48882748	-65.6716461	76	3.98
174899-82-2	[emim][TF ₂ N]	7.89028413	0.58570561	-20.5221665	87	4.48
174899-83-3	[bmim][TF ₂ N]	15.3939532	0.85019842	-49.2274051	119	2.57
382150-50-7	[hmim][TF ₂ N]	8.31146334	0.45883815	-28.4742023	115	3.22
597581-48-1	[b3mpy][BF ₄]	12.0769957	0.57659898	-52.4038887	69	8.86
223437-11-4	[P14][TF ₂ N]	16.0811203	0.85590139	-54.2486521	91	2.50
258273-75-5	[N1114][TF ₂ N]	15.4843608	0.89522148	-48.7547197	76	3.71
					Total:	Average:
					1150	4.62

therefore hypothetical values that have to be estimated using group contribution methods or specific correlations. For the ILs considered in this study, these properties are taken from Valderrama et al. [37–39] and are summarized below (Table 1):

Following Macias-Salinas & Gross [15] the experimental viscosity data were taken from the sources listed in Table 2.

3. Results and discussion

As stated above for the case of ionic liquids for which vapor pressures are very low, experimental viscosity data are limited to liquid state. Thus, in Eq. (4), the gas state contribution of the entropy scaling model is neglected by fixing the parameters b_1 , b_2 and c to zero. It is worth recalling that while b_1 and b_2 enter in the formulation of f_{gas} , c is relative to the sharpness of the transition between f_{dense} and f_{gas} . This reduces the adjustable parameters of the model to a_1 , a_2 and d .

The optimization step of the adjustable coefficients was performed using the BFGS algorithm, a quasi-Newton method. In order to reach the global minimum of the objective function reported in Eq. (11), 10 different optimizations were run, each started from different initial guesses (of a_1 , a_2 and d) generated randomly.

$$F_{\text{obj}} = \frac{1}{N_{\text{data}}} \sum_{i=1}^{N_{\text{data}}} \frac{|\eta_{\text{exp},i} - \eta_{\text{calc},i}|}{\eta_{\text{exp},i}} \quad (11)$$

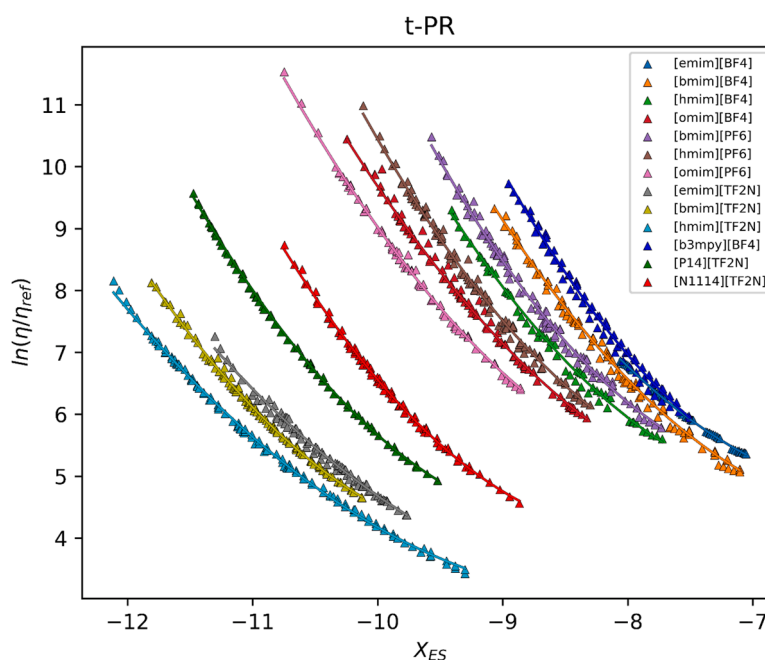
N_{data} is the total number of experimental data points for a given component, $\eta_{\text{calc},i}$ is the calculated value of the viscosity by the entropy scaling model and $\eta_{\text{exp},i}$ is the corresponding experimental value. The resulting optimized parameters and the corresponding average deviations are reported in Tables 3 and 4 for the entropy scaling model combined with each of the two cubic EoS cited before.

From the optimization of the 3 component-dependent coefficients for

Table 4

Model's adjusted parameters for the t-SRK EoS and the corresponding average deviations.

CAS number	IL name	a_1	a_2	d	Number of exp. data points	MAPE%
143314-16-3	[emim][BF4]	8.46479117	0.43567472	-37.4877066	54	1.77
174501-65-6	[bmim][BF4]	8.75538655	0.42908423	-39.5998513	108	7.61
244193-50-8	[hmim][BF4]	12.02888887	0.4771998	-61.6048993	53	7.45
244193-52-0	[omim][BF4]	9.37496072	0.35592265	-52.2984034	101	4.64
174501-64-5	[bmim][PF6]	12.5952649	0.56799263	-56.6851532	93	8.83
304680-35-1	[hmim][PF6]	15.1825542	0.58275319	-76.5462342	108	8.24
304680-36-2	[omim][PF6]	13.9089065	0.48677878	-77.0686945	76	5.33
174899-82-2	[emim][TF2N]	6.86127445	0.48373822	-19.3781716	87	4.90
174899-83-3	[bmim][TF2N]	14.2195322	0.73381332	-49.0774336	119	3.66
382150-50-7	[hmim][TF2N]	7.55474538	0.39469679	-27.7976922	115	3.35
597581-48-1	[b3mpy][BF4]	10.8241832	0.49859882	-49.890201	69	11.10
223437-11-4	[P14][TF2N]	14.8056742	0.74094768	-53.6185844	91	3.92
258273-75-5	[N1114][TF2N]	13.2981251	0.73378214	-44.7644366	76	5.40
					Total:	Average:
					1150	5.81

**Fig. 1.** Results of the entropy scaling model for pure ionic liquids when the translated Peng-Robinson EoS is used. Triangles represent experimental data and solid lines represent calculated data.

each considered chemical species, it appears that the translated Peng-Robinson EoS leads to a slightly better precision than the SRK EoS as reported in Tables 3 and 4. Overall, both the considered equations of state lead to very satisfying correlations that ensure a good reproduction of the experimental data as shown in Figs. 1 and 2.

It is worth recalling that Macias-Salinas and Gross had investigated three different ways to reduce the viscosity: i) use of the macroscopic reduction proposed by Rosenfeld that involves density and temperature; ii) use of the Chapman-Enskog (CE) temperature-dependent relation suited for dilute gas viscosity; iii) and finally, a simple division of the viscosity by its units (i.e., $\eta/(1 \text{ Pa s})$). Summarizing the three models, the most favourable case was achieved with the last approach when the viscosity is divided by unity, resulting in errors as low as 4.47% and 5.28% for the Peng-Robinson and the SRK EoS respectively. On the other hand, the macroscopic and the CE reductions have shown, 4.90% and 5.16% deviations for the PR-EoS and 6.08% and 6.39% deviations for the SRK-EoS respectively. Although these results are similar, it can be

assumed that the slight advantage of the correlation using the viscosity divided by its unit is arbitrary and can be attributed to the limited range of thermodynamic conditions covered by the ionic liquids studied in this article. The superiority of the entropy scaling concept is generally observed when considering a large range of thermodynamic conditions spanning from dilute gases to dense liquids.

This study shows that the general model developed previously for pure fluids, aimed at correlating viscosities over the entire fluid region, can indeed correlate the viscosity of the thirteen ionic liquids in the liquid state with high accuracy. The average deviations between experimental and calculated values are only 4.6% for the t-PR EoS and 5.8% for the t-SRK EoS. Such deviations are similar to those reported in 2023 by Macias-Salinas and Gross who use a less elaborated entropy scaling approach in terms of the proposed correlation function. One of the main advantages of the proposed approach is however that it is not specific to ILs and can be applied to any compound (the reader is referred to our previous paper [16]).

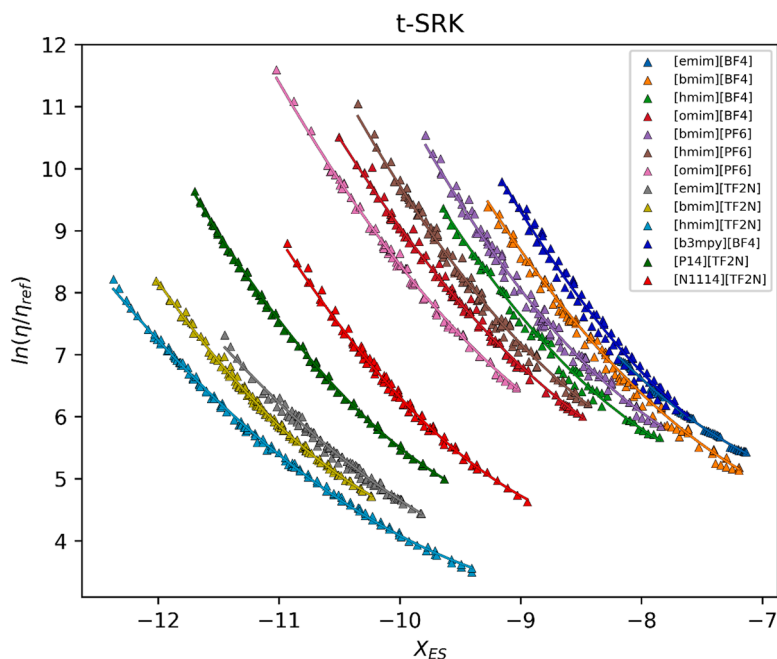


Fig. 2. Results of the entropy scaling model for pure ionic liquids when the translated Soave-Redlich-Kwong EoS is used. Triangles represent experimental data and solid lines represent calculated data.

4. Conclusion

As this short paper shows, the reformulated entropy scaling model previously developed by our group obtains very satisfactory results when applied to pure ionic liquids. This study, which focused solely on the liquid state, demonstrated that the truncated model with only three parameters could accurately correlate experimental viscosities of complex ionic liquids. These results are in line with those obtained by Macías-Salinas and Gross in their recent study.

CRediT authorship contribution statement

Aghilas Dehlouz: Formal analysis, Writing – review & editing. **Romain Privat:** Writing – review & editing, Software. **Jean-Noël Jaubert:** Writing – review & editing, Supervision.

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.

Data availability

Data will be made available on request.

References

- [1] M.B. Shiflett, A.M. Scurto, Ionic liquids: current state and future directions, in: M. B. Shiflett, A.M. Scurto (Eds.), ACS Symposium Series, American Chemical Society, Washington, DC, 2017, pp. 1–13, <https://doi.org/10.1021/bk-2017-1250.ch001>.
- [2] J.P. Hallett, T. Welton, Room-temperature ionic liquids: solvents for synthesis and catalysis. 2, Chem. Rev. 111 (2011) 3508–3576, <https://doi.org/10.1021/cr1003248>.
- [3] J.E. Bara, D.E. Camper, D.L. Gin, R.D. Noble, Room-temperature ionic liquids and composite materials: platform technologies for CO₂ capture, Acc. Chem. Res. 43 (2010) 152–159, <https://doi.org/10.1021/ar9001747>.
- [4] M. Watanabe, M.L. Thomas, S. Zhang, K. Ueno, T. Yasuda, K. Dokko, Application of ionic liquids to energy storage and conversion materials and devices, Chem. Rev. 117 (2017) 7190–7239, <https://doi.org/10.1021/acs.chemrev.6b00504>.
- [5] D.R. MacFarlane, N. Tachikawa, M. Forsyth, J.M. Pringle, P.C. Howlett, G. D. Elliott, J.H. Davis, M. Watanabe, P. Simon, C.A. Angell, Energy applications of

ionic liquids, Energy Environ. Sci. 7 (2014) 232–250, <https://doi.org/10.1039/C3EE42099j>.

- [6] N. Gao, Y. Yang, Z. Wang, X. Guo, S. Jiang, J. Li, Y. Hu, Z. Liu, C. Xu, Viscosity of ionic liquids: theories and models, Chem. Rev. 124 (2024) 27–123, <https://doi.org/10.1021/acs.chemrev.3c00339>.
- [7] G. Shen, C. Held, J.-P. Mikkola, X. Lu, X. Ji, Modeling the viscosity of ionic liquids with the electrolyte perturbed-chain statistical association fluid theory, Ind. Eng. Chem. Res. 53 (2014) 20258–20268, <https://doi.org/10.1021/ie503485h>.
- [8] R. Haghbakhsh, K. Parvaneh, A. Shariati, Viscosities of pure ionic liquids using combinations of free volume theory or friction theory with the cubic, the cubic plus association, and the perturbed-chain statistical associating fluid theory equations of state at high pressures, Ind. Eng. Chem. Res. 56 (2017) 2247–2258, <https://doi.org/10.1021/acs.iecr.6b04193>.
- [9] M. Abolala, K. Peyvandi, F. Varaminian, Modeling the viscosity of pure imidazolium-based ionic liquids using SAFT-VR-Mie EoS, Fluid. Phase Equilib. 394 (2015) 61–70, <https://doi.org/10.1016/j.fluid.2015.02.034>.
- [10] R. Macías-Salinas, Viscosity modeling of ionic liquids using the friction theory and a simple cubic equation of state, Ind. Eng. Chem. Res. 57 (2018) 1109–1120, <https://doi.org/10.1021/acs.iecr.7b04252>.
- [11] R. Macías-Salinas, I.M. Romero-Rueda, Density and viscosity modeling of three deep eutectic solvents using a volume-shifted cubic equation of state coupled with the friction theory, Ind. Eng. Chem. Res. 63 (2024) 718–730, <https://doi.org/10.1021/acs.iecr.3c03478>.
- [12] F. Llovel, L.F. Vega, Assessing ionic liquids experimental data using molecular modeling: [C_mmim][BF₄] case study, J. Chem. Eng. Data 59 (2014) 3220–3231, <https://doi.org/10.1021/je5002472>.
- [13] R. Macías-Salinas, Modified free-volume theory for the viscosity modeling of ionic liquids and deep eutectic solvents, Ind. Eng. Chem. Res. (2024), <https://doi.org/10.1021/acs.iecr.4c00242> acs.iecr.4c00242.
- [14] R. Macías-Salinas, A viscosity model for ionic liquids based on the Eyring's theory and a cubic EoS, J. Mol. Liq. 262 (2018) 161–174, <https://doi.org/10.1016/j.molliq.2018.04.048>.
- [15] R. Macías-Salinas, J. Gross, A viscosity model for pure ionic liquids via the use of a residual-entropy scaling, Fluid. Phase Equilib. 574 (2023) 113897, <https://doi.org/10.1016/j.fluid.2023.113897>.
- [16] A. Dehlouz, R. Privat, G. Galliero, M. Bonnissel, J.-N. Jaubert, Revisiting the entropy-scaling concept for shear-viscosity estimation from cubic and SAFT equations of state: application to pure fluids in gas, liquid and supercritical states, Ind. Eng. Chem. Res. 60 (2021) 12719–12739, <https://doi.org/10.1021/acs.iecr.1c01386>.
- [17] A. Dehlouz, J.-N. Jaubert, G. Galliero, M. Bonnissel, R. Privat, Combining the entropy-scaling concept and cubic- or SAFT equations of state for modelling thermal conductivities of pure fluids, Int. J. Heat. Mass Transf. 196 (2022) 123286, <https://doi.org/10.1016/j.ijheatmasstransfer.2022.123286>.
- [18] A. Dehlouz, J.-N. Jaubert, G. Galliero, M. Bonnissel, R. Privat, Entropy scaling-based correlation for estimating the self-diffusion coefficients of pure fluids, Ind. Eng. Chem. Res. 61 (2022) 14033–14050, <https://doi.org/10.1021/acs.iecr.2c01086>.
- [19] A. Dehlouz, R. Privat, M. Bonnissel, J.-N. Jaubert, An experiment-design methodology for the selection of optimal experimental conditions for the

- correlation of transport properties, *Fluid. Phase Equilib.* 572 (2023) 113829, <https://doi.org/10.1016/j.fluid.2023.113829>.
- [20] A. Dehlouz, R. Privat, G. Galliero, M. Bonnissel, J.-N. Jaubert, Corrigendum to: "revisiting the entropy-scaling concept for shear-viscosity estimation from cubic and SAFT equation of state: application to pure fluids in gas, liquid and supercritical states," *Ind. Eng. Chem. Res.* 63 (2024) 15320–15324, <https://doi.org/10.1021/acs.iecr.4c02705>.
- [21] A. Dehlouz, J.-N. Jaubert, G. Galliero, M. Bonnissel, R. Privat, Corrigendum to: "entropy scaling-based correlation for estimating the self-diffusion coefficients of pure fluids," *Ind. Eng. Chem. Res.* 63 (2024) 15314–15319, <https://doi.org/10.1021/acs.iecr.4c02704>.
- [22] A. Dehlouz, J.-N. Jaubert, G. Galliero, M. Bonnissel, R. Privat, Corrigendum to: "Combining the entropy-scaling concept and cubic- or SAFT equations of state for modelling thermal conductivity of pure fluids," *Int. J. Heat. Mass Transf.* (2024) 126121 <https://doi.org/10.1016/j.ijheatmasstransfer.2024.126121>.
- [23] Y. Rosenfeld, Relation between the transport coefficients and the internal entropy of simple systems, *Phys. Rev. A* 15 (1977) 2545–2549, <https://doi.org/10.1103/PhysRevA.15.2545>.
- [24] Y. Rosenfeld, A quasi-universal scaling law for atomic transport in simple fluids, *J. Phys. Condens. Matter* 11 (1999) 5415–5427, <https://doi.org/10.1088/0953-8984/11/28/303>.
- [25] J.C. Dyre, Perspective: excess-entropy scaling, *J. Chem. Phys.* 149 (2018) 210901, <https://doi.org/10.1063/1.5055064>.
- [26] A. Péneloux, E. Rauzy, R. Fréze, A consistent correction for Redlich-Kwong-Soave volumes, *Fluid. Phase Equilib.* 8 (1982) 7–23, [https://doi.org/10.1016/0378-3812\(82\)80002-2](https://doi.org/10.1016/0378-3812(82)80002-2).
- [27] J.-N. Jaubert, R. Privat, Y.Le Guennec, L. Coniglio, Note on the properties altered by application of a Péneloux-type volume translation to an equation of state, *Fluid. Phase Equilib.* 419 (2016) 88–95, <https://doi.org/10.1016/j.fluid.2016.03.012>.
- [28] R. Privat, J.-N. Jaubert, Y.Le Guennec, Incorporation of a volume translation in an equation of state for fluid mixtures: which combining rule? Which effect on properties of mixing? *Fluid. Phase Equilib.* 427 (2016) 414–420, <https://doi.org/10.1016/j.fluid.2016.07.035>.
- [29] D.-Y. Peng, D.B. Robinson, A New two-constant equation of state, *Ind. Eng. Chem. Fund.* 15 (1976) 59–64, <https://doi.org/10.1021/i160057a011>.
- [30] G. Soave, Equilibrium constants from a modified Redlich-Kwong equation of state, *Chem. Eng. Sci.* 27 (1972) 1197–1203, [https://doi.org/10.1016/0009-2509\(72\)80096-4](https://doi.org/10.1016/0009-2509(72)80096-4).
- [31] A. Pina-Martinez, Y.Le Guennec, R. Privat, J.-N. Jaubert, P.M. Mathias, Analysis of the combinations of property data that are suitable for a safe estimation of consistent T_w - α -function parameters: updated parameter values for the translated-consistent t_c -PR and t_c -RK cubic equations of state, *J. Chem. Eng. Data* 63 (2018) 3980–3988, <https://doi.org/10.1021/acs.jced.8b00640>.
- [32] Y.Le Guennec, R. Privat, J.-N. Jaubert, Development of the translated-consistent t_c -PR and t_c -RK cubic equations of state for a safe and accurate prediction of volumetric, energetic and saturation properties of pure compounds in the sub- and super-critical domains, *Fluid. Phase Equilib.* 429 (2016) 301–312, <https://doi.org/10.1016/j.fluid.2016.09.003>.
- [33] Y.Le Guennec, S. Lasala, R. Privat, J.-N. Jaubert, A consistency test for α -functions of cubic equations of state, *Fluid. Phase Equilib.* 427 (2016) 513–538, <https://doi.org/10.1016/j.fluid.2016.07.026>.
- [34] Y.Le Guennec, R. Privat, S. Lasala, J.-N. Jaubert, On the imperative need to use a consistent α -function for the prediction of pure-compound supercritical properties with a cubic equation of state, *Fluid. Phase Equilib.* 445 (2017) 45–53, <https://doi.org/10.1016/j.fluid.2017.04.015>.
- [35] A. Pina-Martinez, R. Privat, J.-N. Jaubert, D.-Y. Peng, Updated versions of the generalized Soave α -function suitable for the Redlich-Kwong and Peng-Robinson equations of state, *Fluid. Phase Equilib.* 485 (2019) 264–269, <https://doi.org/10.1016/j.fluid.2018.12.007>.
- [36] C.H. Twu, D. Bluck, J.R. Cunningham, J.E. Coon, A cubic equation of state with a new alpha function and a new mixing rule, *Fluid. Phase Equilib.* 69 (1991) 33–50, [https://doi.org/10.1016/0378-3812\(91\)90024-2](https://doi.org/10.1016/0378-3812(91)90024-2).
- [37] J.O. Valderrama, P.A. Robles, Critical properties, normal boiling temperatures, and acentric factors of fifty ionic liquids, *Ind. Eng. Chem. Res.* 46 (2007) 1338–1344, <https://doi.org/10.1021/ie0603058>.
- [38] J.O. Valderrama, R.E. Rojas, Critical properties of ionic liquids, Revisited *Ind. Eng. Chem. Res.* 48 (2009) 6890–6900, <https://doi.org/10.1021/ie900250g>.
- [39] J.O. Valderrama, L.A. Forero, R.E. Rojas, Critical properties and normal boiling temperature of ionic liquids. Update and a new consistency test, *Ind. Eng. Chem. Res.* 51 (2012) 7838–7844, <https://doi.org/10.1021/ie202934g>.
- [40] Y.A. Sammamed, D. González-Salgado, J. Troncoso, L. Romani, A. Baylaucq, C. Boned, Experimental methodology for precise determination of density of RTILs as a function of temperature and pressure using vibrating tube densimeters, *J. Chem. Thermodyn.* 42 (2010) 553–563, <https://doi.org/10.1016/j.jct.2009.11.014>.
- [41] D. Tomida, A. Kumagai, K. Qiao, C. Yokoyama, Viscosity of [bmim][PF6] and [bmim][BF4] at high pressure, *Int. J. Thermophys.* 27 (2006) 39–47, <https://doi.org/10.1007/s10765-006-0020-y>.
- [42] K.R. Harris, M. Kanakubo, L.A. Woolf, Temperature and pressure dependence of the viscosity of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate: viscosity and density relationships in ionic liquids, *J. Chem. Eng. Data* 52 (2007) 2425–2430, <https://doi.org/10.1021/je700370z>.
- [43] A. Ahsosini, A.M. Scurto, Viscosity of imidazolium-based ionic liquids at elevated pressures: cation and anion effects, *Int. J. Thermophys.* 29 (2008) 1222–1243, <https://doi.org/10.1007/s10765-008-0497-7>.
- [44] D. Tomida, S. Kenmochi, T. Tsukada, K. Qiao, Q. Bao, C. Yokoyama, Viscosity and thermal conductivity of 1-hexyl-3-methylimidazolium tetrafluoroborate and 1-octyl-3-methylimidazolium tetrafluoroborate at pressures up to 20 MPa, *Int. J. Thermophys.* 33 (2012) 959–969, <https://doi.org/10.1007/s10765-012-1233-x>.
- [45] K.R. Harris, M. Kanakubo, L.A. Woolf, Temperature and pressure dependence of the viscosity of the ionic liquids 1-methyl-3-octylimidazolium hexafluorophosphate and 1-methyl-3-octylimidazolium tetrafluoroborate, *J. Chem. Eng. Data* 51 (2006) 1161–1167, <https://doi.org/10.1021/je060082s>.
- [46] K.R. Harris, L.A. Woolf, M. Kanakubo, Temperature and pressure dependence of the viscosity of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, *J. Chem. Eng. Data* 50 (2005) 1777–1782, <https://doi.org/10.1021/je050147b>.
- [47] D. Tomida, A. Kumagai, S. Kenmochi, K. Qiao, C. Yokoyama, Viscosity of 1-hexyl-3-methylimidazolium hexafluorophosphate and 1-octyl-3-methylimidazolium hexafluorophosphate at high pressure, *J. Chem. Eng. Data* 52 (2007) 577–579, <https://doi.org/10.1021/je060464y>.
- [48] K.R. Harris, M. Kanakubo, L.A. Woolf, Temperature and pressure dependence of the viscosity of the ionic liquids 1-hexyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, *J. Chem. Eng. Data* 52 (2007) 1080–1085, <https://doi.org/10.1021/je700032n>.
- [49] M. Atilhan, J. Jacquemin, D. Rooney, M. Khraisheh, S. Aparicio, Viscous behavior of imidazolium-based ionic liquids, *Ind. Eng. Chem. Res.* 52 (2013) 16774–16785, <https://doi.org/10.1021/ie403065u>.
- [50] M.E. Kandil, K.N. Marsh, A.R.H. Goodwin, Measurement of the viscosity, density, and electrical conductivity of 1-hexyl-3-methylimidazolium bis(trifluorosulfonyl) imide at temperatures between (288 and 433) K and pressures below 50 MPa, *J. Chem. Eng. Data* 52 (2007) 2382–2387, <https://doi.org/10.1021/je7003484>.
- [51] I. Bandrés, B. Giner, H. Artigas, F.M. Royo, C. Lafuente, Thermophysical comparative study of two isomeric pyridinium-based ionic liquids, *J. Phys. Chem. B* 112 (2008) 3077–3084, <https://doi.org/10.1021/jp077259p>.
- [52] I. Bandrés, R. Alcalde, C. Lafuente, M. Atilhan, S. Aparicio, On the viscosity of pyridinium based ionic liquids: an experimental and computational study, *J. Phys. Chem. B* 115 (2011) 12499–12513, <https://doi.org/10.1021/jp203433u>.
- [53] K.R. Harris, L.A. Woolf, M. Kanakubo, T. Rütther, Transport properties of *N*-Butyl-*N*-methylpyrrolidinium Bis(trifluoromethylsulfonyl)amide, *J. Chem. Eng. Data* 56 (2011) 4672–4685, <https://doi.org/10.1021/je2006049>.
- [54] M. Dakkach, F.M. Gacino, M.J.G. Guimarey, S.K. Mylona, X. Paredes, M.J. P. Comuñas, J. Fernández, M.J. Assael, Viscosity-pressure dependence for nanostructured ionic liquids. Experimental values for butyltrimethylammonium and 1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide, *J. Chem. Thermodyn.* 121 (2018) 27–38, <https://doi.org/10.1016/j.jct.2018.01.025>.