Prediction of molar volume and partial molar volume for CO₂/ionic liquid systems with heterosegmented statistical associating fluid theory

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ABSTRACT

To design ionic liquids (ILs) as effective liquid absorbents for CO₂ separation from flue or synthesis gases, it is necessary to know the properties and phase equilibria of the CO₂/IL systems. The molar volumes of CO₂/IL mixtures are predicted with the heterosegmented statistical associating fluid theory equation of state. The comparison with the available experimental data shows that the model can be used to predict reliably the molar volumes of CO₂/IL mixtures from 293 to 413 K and pressures up to 160 bar. In addition, the partial molar volume of CO₂ in CO₂/IL mixtures and the partial molar volume of CO₂ at infinite dilution in an IL are also predicted.

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1. Introduction

Ionic liquids (ILs) have been the subject of increasing attention due to their unique physicochemical properties such as high thermal stability, large liquid range, high ionic conductivity, high solvating capacity, negligible vapour pressure, and non-flammability that make them ideal solvents for green chemistry. ILs also offer significant cost reduction and environmental benefits because they can be used without losses, in contrast to the volatile organic compounds used nowadays. ILs are often referred to as designer solvents because the cation head, anion, and alkyl chains of an IL can be selected from among a huge diversity to obtain an appropriate IL for a specific purpose.

ILs have shown great potential to be used as liquid absorbents for CO₂ separation from the flue or synthesis gases. To design an effective IL, however, it is necessary to know the CO₂ solubility in IL and the other properties of CO₂/IL mixtures in the liquid phase, such as molar volume (or density), partial molar volume, and partial molar volume at infinite dilution; the partial molar volume of a gas at infinite dilution in an IL is required to describe the influence of pressure on Henry's constant. A growing number of experimental gas solubility data have been reported [1–29] while the molar volume data have been rarely reported so far [1,24,30,31].

Several thermodynamic models have been proposed to represent the molar volume and phase equilibria for pure gas in IL. Vega et al. [32] summarized the work and pointed out that the statistical associating fluid theory (SAFT) equation of state (EOS)-based models were preferred because of the physical background. Recently, SAFT EOS has been extended to describe the gas solubility in ILs [33] where an IL molecule was modelled as a neutral ion pair with one set of parameters or a combination of cation and anion [34]. In the models of hetero-nuclear square-well chain fluids [35] and group contribution equation of state [36], the imidazolium ring-anion pair was modelled as one segment or functional group. As can be concluded, all of these models utilize model parameters that are not completely transferable. Meanwhile, the partial molar volume at infinite dilution and molar volume are seldom investigated and then verified with the available experimental data. Therefore, it is highly desirable to have a model that can predict/represent the phase equilibria and molar volumes, including partial molar volumes, for gas–IL mixtures with transferable parameters. Such a model will enable us to show the effects of alkyl substituents, cation head, and anion of ILs on the phase equilibria and properties of ILs. This could be done by using, for example, a heterosegmented SAFT EOS or group contribution SAFT EOS.

Group contribution SAFT EOS has been developed by different research groups [37–39] but has not been extended to IL-related systems yet. On the other hand, in our previous work, the heterosegmented SAFT has been developed [40] and extended to represent the densities of pure IL and the CO₂ solubility in IL with

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Nomenclature

$\tilde{a}^{res}$	dimensionless residual Helmholtz free energy
$B_{\alpha\beta,i}$	bond fraction of type $\alpha\beta$ in molecule of component i
c_i	constant for calculating $k_{\alpha\beta}$ or u/k
c_{ij}	universal constants listed in Table A1
D_{mn}	universal constants listed in Table A2
$\hat{f}_i^l$	fugacity of component i in the liquid phase
$g_{\alpha\beta}^{SW}$	square-well radial distribution function
k	Boltzmann constant
$k_{\alpha\beta}$	the binary interaction parameter
m	segment number
m_i	the number of segments of component i
MW	molecular weight
n	the number of carbons of n-alkyl
N_{Av}	the Avogadro number
n_B	group bond number
$n(\Gamma_{\alpha i})$	the number of association sites on segment α in molecule of component i
P	pressure in bar
R	the gas constant
T	temperature in Kelvin
u/k	segment energy
u_α	the segment energy of segment α
$u_{\alpha\beta}$	the well depth of square-well potential for the α – β interaction
V	molar volume, cm ³ /mol
$\bar{v}_i^l$	partial molar volume of component i
v^{oo}	segment volume
v_α	the molar volume of segment α
$\bar{v}_{CO_2}^\infty$	partial molar volume of CO ₂ at infinite dilution
x_i	mole fraction of component i
x_α	segment fraction
$X^{A_{\alpha i}}$	mole fraction of molecule of component i not bonded at side A of segment α
ε	well depth of the association site–site potential
$\hat{\phi}_i^l$	fugacity coefficient of component i in the liquid phase
κ	parameter related to the volume available for bonding
λ	segment reduced range of the potential well
$\lambda_{\alpha\beta}$	the reduced range of the potential well for the α – β interaction
ρ_m	molar density
ρ_n	number density
ρ^*	reduced density
σ_α	the diameter of segment α
$\sigma_{\alpha\beta}$	distance between centers of segment α and β at contact
τ	close-packed reduced density ($=2^{1/2}\pi/6$)
$\Delta^{A_{\alpha i}B_{\beta j}}$	association strength between site A_α at molecule of component i and site B_β at molecule of component j

a set of transferable parameters for alkyl substituents, cation head, and anion of IL [41,42]. In the present study, this heterosegmented SAFT EOS will be used to predict the molar volumes of CO₂/IL mixtures, the partial molar volumes of CO₂ in CO₂/IL mixtures, and the partial molar volume of CO₂ at infinite dilution in an IL. The ILs investigated are imidazolium-based ILs, i.e., [C_nmim][Tf₂N], [C_nmim][BF₄], and [C_nmim][PF₆].

2. Molecular model and theory

The detailed description of the molecular model and theory are given in our previous work [41,42], and only a brief summary is given.

2.1. Theory

The IL molecule is divided into several groups representing the alkyls, cation head, and anion. The cation of IL is modelled as a heterosegmented chain molecule that consists of the cation head represented by one effective segment and groups of segments of different types representing different substituents (alkyls). Each group has five parameters, i.e., segment number m , segment volume v^{oo} , segment energy u/k , the reduced range of the potential well λ , and group bond number n_B , which is the effective number of bonds contributed by the group and used to calculate the bond fraction in the chain term. We note that our description of the cation head in our previous publications [41,42] was not accurate. In fact, the cation head is a short chain with an effective number of segments of one. Unlike cation, the anion of IL is represented by a single spherical segment, not a chain molecule, and thus its group bond number is zero (no chain term for the anion).

To account for the electrostatic/polar interaction between the cation and anion, the cation head and anion each have one association site, which can only cross associate to each other. Two additional parameters, i.e., the well depth of the association site-site potential ε and the parameter related to the volume available for bonding κ are used to describe this cross association [41].

CO₂ is modelled as a molecule with one type of segment having three association sites, two sites of type O and one site of type C, where sites of the same type do not associate with each other [42].

For the CO₂/IL systems, we assign another type of association site in the anion of IL and allow cross association between this association site and site of type C in CO₂ to account for this Lewis acid–base interaction. Since the available experimental data [43] reveals that the content of IL in the vapor phase is very low at the temperature and pressure of interest, in this work we assume that IL exists only in the liquid phase [42].

With the framework of heterosegmented SAFT, the dimensionless residual Helmholtz free energy is defined as follows:

$$\tilde{a}^{res} = \tilde{a}^{hs} + \tilde{a}^{disp} + \tilde{a}^{chain} + \tilde{a}^{assoc} \quad (1)$$

where the superscripts on the right side refer to terms accounting for the hard-sphere, dispersion, chain, and association interactions, respectively. The detailed expressions required for the individual terms in Eq. (1) are given in Refs. [40,41,44–46] and summarized in Appendix A for completeness.

2.2. Model parameters

All of the needed model parameters were obtained from our previous works, as briefly described below. In this work, these parameters are used without any adjustment.

2.3. Parameters for pure CO₂

The parameters of pure CO₂ were fitted to its vapour pressure and saturated liquid density from 218 to 302 K [42]. The parameters fitted are listed in Table 1.

2.4. Parameters for pure IL

The parameters of alkyls were estimated directly from those for n-alkanes [44]. The segment number and bond number were calculated from $m = (n + 1)/3$ and $n_B = (2n - 1)/6$, respectively, and the

Table 1
Parameters for CO₂ [42].

Parameter	Value	Parameter	Value
m	1.3513	λ	1.422
ν^{oo} , cm ³ /mol	11.137	ε^{CO}/k , K	217.7834
u^0/k , K	219.992	κ^{CO}	0.18817

Table 2
Parameters ν^{oo} , u/k , and λ for alkyls [41].

n	MW (g/mol)	ν^{oo} (cm ³ /mol)	u/k (K)	λ
1	15.035	16.9740	194.6721	1.5628
2	29.062	19.7362	227.0978	1.5666
3	43.088	21.1998	238.8779	1.5846
4	57.115	21.8387	247.2764	1.5897
5	71.142	22.4333	253.2574	1.5897
6	85.169	22.8280	256.9062	1.5910
7	99.196	23.1253	259.1726	1.5926
8	113.222	23.4905	262.1160	1.5908
9	127.249	23.4833	267.4389	1.5832
11	155.303	23.9364	271.5238	1.5802
13	183.356	24.1598	271.7395	1.5829
15	211.410	24.1988	271.0103	1.5872
19	267.517	24.4288	273.4217	1.5865

parameters ν^{oo} , u/k , and λ were then estimated, which are listed in Table 2. The parameters are well behaved against the molecular weight (MW) of alkyl and can be represented by the following equations:

$$\begin{cases} m\nu^{oo} = 0.600713 \text{ MW} + 2.22445 \\ m\frac{u}{k} = 6.72171 \text{ MW} + 29.6527 \\ m\lambda = 0.0377047 \text{ MW} + 0.48767 \end{cases} \quad (2)$$

Parameters for groups representing cation head (imidazolium cation head (imi⁺)) and anions (Tf₂N[−], BF₄[−], and PF₆[−]), including the two association parameters, were fitted to a group of experimental liquid densities of ILs ([C₂mim][Tf₂N], [C₇mim][Tf₂N], [C₈mim][Tf₂N], [C₂mim][BF₄], [C₄mim][BF₄], [C₈mim][BF₄], [C₄mim][PF₆], [C₆mim][PF₆], and [C₈mim][PF₆]) from 293.15 to 398.15 K and up to 400 bar [41]. The parameters fitted are summarized in Table 3. As shown in Table 3, the cation tends to have a large λ value, while anions tend to have small λ values. In fact, we did not expect the cation to have a large λ value because we did not explicitly treat the long-range electrostatic interaction in our model. However, it is interesting to note that the same λ trends were also observed in our previous works on inorganic salts [44,47,48].

With the fitted parameters, the densities of [C_{*n*}mim][Tf₂N], [C_{*n*}mim][BF₄], and [C_{*n*}mim][PF₆], in which n ranges from 2 to 8, were compared with other available experimental data, and the model was found to well represent the densities of these ionic

Table 3
Parameters for imidazolium cation head (imi⁺), Tf₂N[−], BF₄[−], and PF₆[−] [41].

	imi ⁺	Tf ₂ N [−]	BF ₄ [−]	PF ₆ [−]
ν^{oo} (cm ³ /mol)	22.1794	78.7377	22.7970	34.9781
λ	2.3089	1.6373	1.1014	1.1071
n_B	1.2922	0	0	0
c_1^a (K)	1007.7533	1048.7711	352.2533	−344.5960
c_2^a	−8.595206	−1.882762	−0.768297	4.477235
c_3^a (K ^{−1})	0.0260940286	−	−	−
ε (K)	1633.7442	1788.8889	1208.1711	8873.4790
$10^4\kappa$	2.060446	2.423795	5.203447	52.882628

^a These constants are used to calculate the temperature-dependent segment energy of cation head and anion:

$$\frac{u}{k} = \begin{cases} c_1 + c_2 \cdot T + c_3 \cdot T^2 & \text{cation head} \\ c_1 + c_2 \cdot T & \text{anion} \end{cases}$$

Table 4
Parameters fitted for (CO₂ + imidazolium-based IL) [42].

	ε_L	κ_L
C-Tf ₂ N	894.1751	0.057747
C-BF ₄	1298.5604	0.040840
C-PF ₆	1057.0701	0.190719

	c_1^a	$10^4 c_2$ (K ^{−1}) ^a	$10^6 c_3$ (K ^{−2}) ^a
CO ₂ -imi	0.4733	−5.73946	−1.25361
CO ₂ -Tf ₂ N	1.6140	−97.23875	15.94551
CO ₂ -BF ₄	0.0715	10.39087	−3.19146
CO ₂ -PF ₆	−0.5315	33.70713	−8.42553
CO ₂ -methyl	−0.0802	−	−
CO ₂ -ethyl	0.0061	−	−
CO ₂ -butyl	0.0166	−	−
CO ₂ -hexyl	0.0690	−	−
CO ₂ -octyl	0.0546	−	−

^a These constants are used to calculate $k_{\alpha\beta}$ in Eq. (A10).

liquids from 293.15 to 415 K and up to 650 bar, and well capture the effects of temperature, pressure, and alkyl types on densities [41].

2.5. Cross parameters between CO₂ and IL

To describe the CO₂ solubility in the imidazolium-based IL, temperature-dependent cross parameters were allowed to adjust the dispersion energy between segments of CO₂ and cation head ($k_{\text{CO}_2\text{-cation head}}$) or anion ($k_{\text{CO}_2\text{-anion}}$), while temperature independent cross parameters were used to adjust the dispersion energy between segments of CO₂ and alkyl ($k_{\text{CO}_2\text{-alkyl}}$) [42]. The binary interaction parameters $k_{\text{CO}_2\text{-alkyl}}$, $k_{\text{CO}_2\text{-cation head}}$, and $k_{\text{CO}_2\text{-anion}}$ along with the cross association parameters ε_L and κ_L were fitted to the CO₂ solubility in [C₂mim][Tf₂N], [C₄mim][Tf₂N], [C₆mim][Tf₂N], [C₈mim][Tf₂N], [C₂mim][BF₄], [C₄mim][BF₄], [C₆mim][BF₄], [C₈mim][BF₄], [C₄mim][PF₆], [C₆mim][PF₆], and [C₈mim][PF₆] from 283 to 415 K and at both low pressures and elevated pressures up to 200 bar [42]. The fitted parameters are listed in Table 4.

It is worth mentioning that for any heterosegmented model, the number of parameters seems to be excessive, but we need to realize that those parameters are transferable. In this work, the number of parameters to describe a group of ionic liquids is in fact smaller than those of homosegmented models. For example, let us consider all ionic liquids that can be formed by combining 1 cation head, 3 different anions, and 4 different alkyls. The number of ionic liquids is $1 \times 3 \times 4 = 12$ and in our heterosegmented model, the number of parameters needed to describe this group is 1×8 (cation head) + 3×6 (anion) + 4×3 (alkyl) = 38. In a homosegmented model that requires only 5 parameters to describe an ionic liquid, the number of parameters needed for that group would be $12 \times 5 = 60$, which is far exceeding that in our model. The same for the constants of the binary interaction parameters in this work, they are transferable to any ionic liquid having that alkyl/cation head/anion.

3. Results and discussions

3.1. Molar volume

The molar volume V , cm³/mol, for the systems of CO₂-imidazolium-based IL has been measured by several research groups. Blanchard et al. [24] measured the molar volumes for CO₂-[C₄mim][PF₆], CO₂-[C₈mim][PF₆], and CO₂-[C₈mim][BF₄] at 313.15, 323.15, and 333.15 K and at pressures up to 110 bar. Aki et al. [1] measured the molar volumes for the systems of

Fig. 1. Molar volume of CO_2 -[C₄mim][Tf₂N] at 333, 313, and 298 K (from top to bottom). $\circ$, $\diamond$, and $+$, exp. data [1]; —, predicted.

Fig. 2. Molar volume of CO_2 -[C₈mim][Tf₂N] at 333, 313, and 298 K (from top to bottom). $\circ$, $\diamond$, and $+$, exp. data [1]; —, predicted.

CO_2 -[C₄mim][BF₄], CO_2 -[C₄mim][PF₆], CO_2 -[C₄mim][Tf₂N], CO_2 -[C₆mim][Tf₂N], and CO_2 -[C₈mim][Tf₂N] at 298, 313, and 333 K and at pressures up to 150 bar. Kumelan et al. [30] also measured the molar volumes of CO_2 -[C₆mim][Tf₂N] at 293.15, 333.15, 373.2, and 413.2 K and at pressures up to 100 bar. The densities of CO_2 -[C₆mim][Tf₂N] were also determined by Ren and Scurto [31] at 333.15 K and up to 125 bar.

With the parameters obtained from pure component data and those from CO_2 solubility data in IL, the model is used to predict the molar volume, which is then compared with the available experimental data. Figs. 1 and 2 show the comparison for systems of CO_2 -[C₄mim][Tf₂N] and CO_2 -[C₈mim][Tf₂N], respectively, with agreement throughout the whole temperature and pressure range. The comparison results for CO_2 -[C₆mim][Tf₂N] system are shown in Fig. 3. At 333 K, the experimental data are from three sources [1,30,31] and there is some inconsistency among these sources, while the calculation results agree well with the experimental data of [30]. At other temperatures (293, 298, 313, 373, and 413 K), the

calculation results agree well with experimental data throughout the whole pressure range.

The calculated and experimental molar volumes for CO_2 -[C₄mim][BF₄] at 298, 313, and 333 K are depicted in Fig. 4. At 313 K, the calculated results agree well with the experimental data, while at other two temperatures, the calculated results are not as good as that at 313 K. The calculated result is slightly higher than the experimental data at 298 K, while it is lower than the experimental data at 333 K in a certain pressure range. As we know that when the pressure goes to zero, the solubility of CO_2 goes to a very small value or zero, and the molar volume of the solution reduces to that of pure IL. From Fig. 4, we can see that the predicted molar volume of pure IL is also lower than the experimental data, and that may be one of the reasons for the discrepancies between the experimental and calculated molar volumes at 333 K for this system.

For CO_2 -[C₄mim][PF₆] system, the comparison of the prediction is illustrated in Fig. 5, in which the experimental data are from Aki et al. [1] and Blanchard et al. [24]. As shown in Fig. 5(a), at 298 and

Fig. 3. Molar volume of CO_2 -[C₆mim][Tf₂N]: (a) at 333, 313, and 298 K (from top to bottom). $\circ$, $\diamond$, and $+$, exp. data [1]; $\triangle$, exp. data [30]; $\times$, exp. data [31]; —, predicted; (b) at 413.2, 373.2, 333.15, and 293.15 K (from top to bottom). $\times$, $\circ$, $\triangle$, and $\diamond$, exp. data [30]; —, predicted.

Fig. 4. Molar volume of CO₂–[C₄mim][BF₄] at 333, 313, and 298 K (from top to bottom). ○, ◇, and +, exp. data [1]; —, predicted.

333 K, the predicted results agree extremely well with the available experimental data, while at 313 K and high pressures, the predicted results are slightly higher than the experimental data. It was stated in [1] that at 313 K, the uncertainty of experimental data at high pressures could be $\pm 9 - 12 \text{ cm}^3/\text{mol}$, which was much larger than that at low pressures and at other temperatures. The uncertainty for most of the other data points was less than $\pm 4 \text{ cm}^3/\text{mol}$.

For CO₂–[C₄mim][PF₆] system, it has been stated that the CO₂ solubilities from Blanchard et al. [24] are not reliable [1], but no discussion on the corresponding molar volume data. From Fig. 5, it can be seen that the experimental molar volumes from Blanchard et al. [24] at 333.15 and 313.15 K are much lower than those from Aki et al. [1] and the predicted results of this work. At 323.15 K, the experimental data are also lower than the predicted molar volumes. Therefore, we can conclude that the molar volume data from Blanchard et al. [24] are not reliable either.

The comparison of the predicted molar volumes to the experimental data from Blanchard et al. [24] for CO₂–[C₈mim][PF₆], and CO₂–[C₈mim][BF₄] is shown in Fig. 6. The agreement is not good

for both systems. Since no other experimental molar volume data is available, we cannot verify which is unreliable, the experimental data or the predicted result.

3.2. Partial molar volume

Experimental research has revealed that the partial molar volume of CO₂ in an IL is much smaller than that observed in most solvents. In this work, the model is used to predict the partial molar volumes of CO₂ in CO₂/IL mixtures. There are two options that can be chosen for calculating the partial molar volume of a component in a binary mixture, i.e., using the fugacity of that component at constant T and x (method 1) or using the molar volume of the mixture at constant T and P (method 2). In method 1, the partial molar volume of component i at any composition is calculated from:

$$\bar{v}_i^l = RT \left(\frac{\partial \ln(\hat{f}_i^l)}{\partial P} \right)_{T,x} \quad (3)$$

where $\hat{f}_i^l$ is the fugacity of component i in the liquid phase, and the derivative term is calculated numerically, i.e.:

$$\bar{v}_i^l = RT \left(\frac{1}{P} + \frac{\ln(\hat{\phi}_i^l)_{P+\Delta P} - \ln(\hat{\phi}_i^l)_{P-\Delta P}}{2 \Delta P} \right)_{T,x} \quad (4)$$

where $\hat{\phi}_i^l$ is the fugacity coefficient of component i in the liquid phase, R is the gas constant, T is the absolute temperature, and P is the pressure in bar.

In method 2, the partial molar volume of component i at any composition is calculated from:

$$\bar{v}_i^l = \left(V|_{x_i} + \frac{\partial V}{\partial x_i} \bigg|_{x_i} \cdot (1 - x_i) \right)_{T,P} \quad (5)$$

where x_i is the mole fraction of component i , $V|_{x_i}$ is the molar volume of the mixture at that composition, and $\partial V/\partial x_i$ is the first derivative of V with respect to x_i evaluated at that composition, which is also calculated numerically, i.e.:

$$\left(\frac{\partial V}{\partial x_i} \right)_{T,P} = \left(\frac{V_{x_i+\Delta x_i} - V_{x_i-\Delta x_i}}{2 \Delta x_i} \right)_{T,P} \quad (6)$$

To calculate the partial molar volume at equilibrium, the equilibrium composition is calculated at a certain temperature and

Fig. 5. Molar volume of CO₂–[C₄mim][PF₆]: (a) at 333, 313, and 298 K (from top to bottom). ○, ◇, and +, exp. data [1]; —, calculated; (b) at 333.15, 323.15, and 313.15 K (from top to bottom). ◇, ○, and +, exp. data [24]; —, predicted.

Fig. 6. Molar volume for: (a) CO₂–[C₈mim][BF₄]; (b) CO₂–[C₈mim][PF₆] at 333.15, 323.15, and 313.15 K (from top to bottom). $\diamond$, $\circ$, and $+$, exp. data [53]; —, predicted.

pressure first, and then the partial molar volume is calculated at a certain temperature, pressure, and equilibrium composition.

Theoretically, both of these two methods can be used to predict $\bar{v}_i^l$. However, for method 1, a small difference in the derivative term will cause a large difference in $\bar{v}_i^l$ because of the magnitude of the RT term. Because of this reason, it is difficult to obtain reliable results from method 1. On the other hand, method 2 does not have such a problem.

To illustrate the problem, $\bar{v}_{\text{CO}_2}^l$ in [C₄mim][PF₆] at a concentration of 10 mol% CO₂ ($x_{\text{CO}_2} = 0.1$) at 298.2, 313.3, and 333.3 K is predicted using the two methods, and the results are listed in Table 5. In method 1, the value of the derivative term $[\partial \ln(\hat{\phi}_i^l)/\partial P = (\ln(\hat{\phi}_i^l)_{P+\Delta P} - \ln(\hat{\phi}_i^l)_{P-\Delta P})/2\Delta P]$ is different slightly with different choices of ΔP , but this slight difference in the derivative term results in completely different results in $\bar{v}_{\text{CO}_2}^l$. At $T = 298.2$ K, $P = 5.68$ bar, and $x_{\text{CO}_2} = 0.1$, $\bar{v}_{\text{CO}_2}^l$ is 35.8 cm³/mol with $\Delta P = 1.0 \times 10^{-3} P$ while it is 18.3 cm³/mol with $\Delta P = 1.0 \times 10^{-6} P$, and the corresponding values of the derivative terms are 0.174613 and 0.175319 bar⁻¹, respectively. In addition, for the case listed in Table 5, it is obvious that $\Delta P \leq 1.0 \times 10^{-5} P$ cannot be used in Eq. (4) to obtain $\bar{v}_{\text{CO}_2}^l$ in [C₄mim][PF₆].

The $\bar{v}_{\text{CO}_2}^l$ calculated using method 2 at the same conditions is also listed in Table 5. Different values of Δx_i are chosen ($1.0 \times 10^{-4} x_i$, $1.0 \times 10^{-5} x_i$, and $1.0 \times 10^{-6} x_i$) to investigate the effect of Δx_i on $\bar{v}_{\text{CO}_2}^l$ calculated using Eqs. (5) and (6). It is found that the same $\bar{v}_{\text{CO}_2}^l$ is obtained with different Δx_i . The comparison of the results obtained from the two methods also shows that the results of $\bar{v}_{\text{CO}_2}^l$ using method 1 with $\Delta P = 1.0 \times 10^{-3} P$ are the same as those using method 2.

To investigate method 1 further, $\bar{v}_{\text{CO}_2}^l$ in [C₄mim][PF₆] is calculated throughout the whole temperature and pressure range studied by Aki et al. [1] using different values of ΔP ($1.0 \times 10^{-2} P$, $1.0 \times 10^{-3} P$, $1.0 \times 10^{-4} P$, and $1.0 \times 10^{-5} P$). Again, the difference in $\partial \ln(\hat{\phi}_i^l)/\partial P$ is small, but the difference in $\bar{v}_{\text{CO}_2}^l$ is significant, especially in the lower pressure range. Moreover, the $\bar{v}_{\text{CO}_2}^l$ calculated using method 1 with $\Delta P = 1.0 \times 10^{-3} P$ extremely agrees with that calculated using method 2 as shown in Fig. 7.

Based on the above comparison, we recommend to use method 2 to obtain $\bar{v}_i^l$, and this method is used for the rest of this work. In the case where method 1 is chosen to obtain $\bar{v}_i^l$, we should be very careful about the choice of ΔP .

By using molecular dynamics simulations, $\bar{v}_{\text{CO}_2}^l$ in [C₄mim][PF₆] at a concentration of 10 mol% CO₂ was predicted to be 33 cm³/mol

[49]. In the same work, it was also mentioned that the partial molar volumes of CO₂ at CO₂ mol fractions below 0.49 were estimated using the experimental data and found to be nearly constant at 29 cm³/mol.

For the same system, the $\bar{v}_{\text{CO}_2}^l$ predicted in this work varies slightly in the range of 35.3–36.8 cm³/mol throughout the whole temperature and pressure range studied by Aki et al. [1]. At 10 mol% of CO₂, the values of $\bar{v}_{\text{CO}_2}^l$ at 298.2, 313.3, and 333.3 K and at the corresponding saturated pressures of 5.68, 7.49, and 10.45 bar are 35.8, 35.6, and 35.3 cm³/mol, respectively, which are listed in Table 5.

The prediction of the partial molar volumes of CO₂ in [C₄mim][PF₆] at the specified conditions and composition in this work are higher than that predicted with molecular dynamics simulations, and higher than those estimated from experimental data. However, we should mention that the molar volumes for different systems predicted in this work agree with the experimental data from different sources, as shown in the previous section.

Fig. 7. Partial molar volume of CO₂ in [C₄mim][PF₆] at 298.2, 313.3, and 333.3 K (from top to bottom). $+$, $\diamond$, and $\circ$, calculated with Eq. (14) with $\Delta P = 1.0 \times 10^{-3} P$; —, calculated using Eqs. (15) and (16).

Table 5
 $\bar{v}_{\text{CO}_2}^l$ in [C₄mim][PF₆] at $x_{\text{CO}_2} = 1.1 \text{ cm}^3/\text{mol}$.

T, K	P, bar	Method 1								Method 2 $\bar{v}_{\text{CO}_2}^l$
		$\Delta P = 1.0 \times 10^{-3} P$		$\Delta P = 1.0 \times 10^{-4} P$		$\Delta P = 1.0 \times 10^{-5} P$		$\Delta P = 1.0 \times 10^{-6} P$		
		$\bar{v}_{\text{CO}_2}^l$	$-\partial \ln(\hat{\phi}_i^l)/\partial P$	$\bar{v}_{\text{CO}_2}^l$	$-\partial \ln(\hat{\phi}_i^l)/\partial P$	$\bar{v}_{\text{CO}_2}^l$	$-\partial \ln(\hat{\phi}_i^l)/\partial P$	$\bar{v}_{\text{CO}_2}^l$	$-\partial \ln(\hat{\phi}_i^l)/\partial P$	
298.2	5.68	35.8	0.174613	35.9	0.174610	37.2	0.174555	18.3	0.175319	35.8
313.3	7.49	35.6	0.132147	35.6	0.132146	36.4	0.132114	27.8	0.132443	35.6
333.3	10.45	35.3	0.094419	35.3	0.094420	35.6	0.094408	30.9	0.094580	35.3

3.3. Partial molar volume of CO₂ at infinite dilution

The partial molar volume of a gas *i* that is dissolved at high dilution in a solvent is needed to describe the influence of pressure on Henry's constant, and it is defined as:

$$\bar{v}_i^\infty = V|_{x_i=0} + \left(\frac{\partial V}{\partial x_i} \right)_{T,P} \bigg|_{x_i=0} \quad (7)$$

where *V* is the molar volume and $(\partial V/\partial x_i)_{T,P}|_{x_i=0}$ is calculated by using the forward finite difference, i.e.:

$$\left(\frac{\partial V}{\partial x_i} \right)_{T,P} \bigg|_{x_i=0} = \left(\frac{V_{x_i=\Delta x_i} - V_{x_i=0}}{\Delta x_i} \right)_{T,P} \quad (8)$$

The predicted $\bar{v}_{\text{CO}_2}^\infty$ in [C₆mim][Tf₂N] at different temperatures and pressures is listed in Table 6. The $\bar{v}_{\text{CO}_2}^\infty$ in [C₆mim][Tf₂N] increases with increasing temperature and decreases with increasing pressure.

A reliable $\bar{v}_{\text{CO}_2}^\infty$ is usually derived from volumetric measurements. However, volumetric data are rarely obtained. Moreover, the measured volumetric data are those under equilibrium conditions instead of at constant temperature and pressure, i.e., the available experimental volumetric data are those measured at a certain temperature, pressure, and the corresponding equilibrium composition or at a certain temperature, composition, and the corresponding saturated pressure. Based on the measured volumetric data under equilibrium conditions and the assumption that the effect of pressure on volumetric data is negligible, $\bar{v}_{\text{CO}_2}^\infty$ in [C₆mim][Tf₂N] was estimated by Kumelan et al. [30] and also listed in Table 6 for comparison.

There are some discrepancies between the results derived from experimental volumetric data and those from the model prediction. To find out the reasons, the predicted and experimental volume *V* (volume of solution per one kg IL, cm³/kg IL) as a function of molality of CO₂ at equilibrium pressure is depicted in Fig. 8. In the work of Kumelan et al. [30], the $\bar{v}_{\text{CO}_2}^\infty$ was the slope of the fitting linear curve to the experimental *V* vs. *m*_{CO₂} data at each temperature.

Fig. 8 shows that the predicted volume *V* is lower than the experimental data at each temperature, while from Fig. 3(b) it is shown that the molar volume prediction is consistent with experimental data at different temperatures and pressures. These observations

Fig. 8. Volume *V_m* (cm³/kg IL) of CO₂–[C₆mim][Tf₂N] at 413.2, 373.2, 333.15, and 293.2 K (from top to bottom). Δ, ○, +, and ◇, exp. data [30]; —, predicted. ---, linear fitting from experimental data.

imply that there are some discrepancies between the equilibrium composition predicted with the model and that measured experimentally at a certain temperature and pressure. Thus, the discrepancy in $\bar{v}_{\text{CO}_2}^\infty$ in Table 6 is partly due to this reason. Furthermore, the assumption that the pressure effect is negligible in obtaining $\bar{v}_{\text{CO}_2}^\infty$ from the experimental data and the inaccuracy in predicting the volume of pure IL from our model could be other reasons to cause the discrepancy.

The $\bar{v}_{\text{CO}_2}^\infty$ in other ILs of course can be predicted with the model. However, there is no experimental data available, and the comparison cannot be performed.

4. Conclusion

Heterosegmented SAFT EOS is used to predict the molar volumes of CO₂/IL mixtures. The comparison with the experimental data shows that the molar volumes are predicted reliably from 293 to 413 K and pressures up to 160 bar. The partial molar volumes of CO₂/IL mixtures and the partial molar volumes of CO₂ at infinite dilution in an IL are also predicted and compared with those estimated from volumetric data or that predicted using molecular dynamics simulations, but due to the scarcity of the available data derived from experiments, the model prediction cannot be verified rigorously.

Table 6
 $\bar{v}_{\text{CO}_2}^\infty$ in [C₆mim][Tf₂N], cm³/mol.

Pressure, bar	Temperature, K			
	293.15	333.15	373.2	413.2
1	37.32	37.67	38.47	39.56
5	37.27	37.63	38.43	39.52
10	37.21	37.58	38.38	39.47
15	37.16	37.52	38.33	39.42
20	37.10	37.47	38.28	39.37
50	36.77	37.17	37.99	39.08
100	36.25	36.69	37.54	38.63
From volumetric data [30]	39.4	41.8	43.9	44.0

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Appendix A. Heterosegmented SAFT EOS

With the framework of heterosegmented SAFT, the dimensionless residual Helmholtz free energy is defined as follows:

$$\tilde{a}^{\text{res}} = \tilde{a}^{\text{hs}} + \tilde{a}^{\text{disp}} + \tilde{a}^{\text{chain}} + \tilde{a}^{\text{assoc}} \quad (\text{A1})$$

where the superscripts on the right side refer to terms accounting for the hard-sphere, dispersion, chain, and association interactions, respectively. In the expression of each term below, for CO₂/IL systems, the word ‘component’ refers to CO₂, anion, or cation of IL.

A.1. Hard-sphere term $\tilde{a}^{\text{hs}}$

The hard-sphere contribution $\tilde{a}^{\text{hs}}$ in heterosegmented SAFT is given by [40]

$$\tilde{a}^{\text{hs}} = \frac{6}{\pi N_{\text{Av}} \rho_m} \left[\frac{(\zeta_2)^3 + 3\zeta_1 \zeta_2 \zeta_3 - 3\zeta_1 \zeta_2 (\zeta_3)^2}{\zeta_3 (1 - \zeta_3)^2} - \left(\zeta_0 - \frac{(\zeta_2)^3}{(\zeta_3)^2} \right) \ln(1 - \zeta_3) \right] \quad (\text{A2})$$

where N_{Av} is the Avogadro number, ρ_m is the molar density, and

$$\zeta_k = \frac{\pi}{6} N_{\text{Av}} \rho_m \sum_i X_i m_i \sum_{\alpha} x_{\alpha} (\sigma_{\alpha})^k \quad (k = 0, 1, 2, 3) \quad (\text{A3})$$

where X_i is the mol fraction of component i , m_i is the number of segments of component i , σ_{α} is the diameter of segment α , and x_{α} is the segment fraction defined as

$$x_{\alpha} = \frac{\text{number of moles of segments } \alpha}{\text{number of moles of all segments}} \quad (\text{A4})$$

A.2. Dispersion term $\tilde{a}^{\text{disp}}$

The dispersion term is calculated from [40,44,50,51]:

$$\tilde{a}^{\text{disp}} = \sum_i X_i m_i \left[\frac{1}{k_B T} a_1^{\text{disp}} + \frac{1}{(kT)^2} a_2^{\text{disp}} + \tilde{a}^t \right] \quad (\text{A5})$$

where k is the Boltzmann constant, T is the temperature in Kelvin, and

$$a_1^{\text{disp}} = \sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} a_{1,\alpha\beta}^{\text{disp}} \quad (\text{A6})$$

where α and β are the segment types, and $a_{1,\alpha\beta}^{\text{disp}}$ is the first-order binary term for α – β segment interaction given by

$$a_{1,\alpha\beta}^{\text{disp}} = -4 \left(\frac{\pi}{6} \sigma_{\alpha\beta}^3 N_{\text{Av}} \rho_m \right) u_{\alpha\beta} (\lambda_{\alpha\beta}^3 - 1) g_{\alpha\beta}^{\text{hs}}(\sigma_{\alpha\beta}, \zeta_{3,\text{eff}}) \quad (\text{A7})$$

In Eq. (A7), $\sigma_{\alpha\beta}$ is the distance between centers of segment α and β at contact, $u_{\alpha\beta}$ is the well depth of square-well potential for the α – β interaction, and $\lambda_{\alpha\beta}$ is the reduced range of the potential well for the α – β interaction. The combining rules used for $\sigma_{\alpha\beta}$ and $u_{\alpha\beta}$ are

$$\sigma_{\alpha\beta} = \frac{1}{2}(\sigma_{\alpha} + \sigma_{\beta}) \quad (\text{A8})$$

$$u_{\alpha\beta} = u_{\beta\alpha} = \sqrt{u_{\alpha} u_{\beta}} (1 - k_{\alpha\beta}) \quad (\text{A9})$$

where u_{α} is the segment energy of segment α , and $k_{\alpha\beta}$ is the binary interaction parameter which can be temperature-dependent or temperature-independent, i.e.:

$$k_{\alpha\beta} = \begin{cases} c_1 + c_2 T + c_3 T^2 & \text{CO}_2\text{--cation head or CO}_2\text{--anion} \\ c_1 & \text{CO}_2\text{--alkyl} \end{cases} \quad (\text{A10})$$

In Eq. (A10), c_1 , c_2 , and c_3 are constants for calculating $k_{\alpha\beta}$.

A simple arithmetic-mean combining rule is used for $\lambda_{\alpha\beta}$, analogous to that for the segment diameters:

$$\lambda_{\alpha\beta} = \frac{1}{2}(\lambda_{\alpha} + \lambda_{\beta}) \quad (\text{A11})$$

where λ_{α} is the reduced range of the potential well of segment α .

The radial distribution function for a mixture of hard spheres in Eq. (A7) is calculated using Carnahan–Starling’s equation but evaluated at the effective reduced variable $\zeta_{k,\text{eff}}$:

$$g_{\alpha\beta}^{\text{hs}}(\sigma_{\alpha\beta}, \zeta_{3,\text{eff}}) = \frac{1}{1 - \zeta_{3,\text{eff}}} + \frac{3\sigma_{\alpha}\sigma_{\beta}}{\sigma_{\alpha} + \sigma_{\beta}} \frac{\zeta_{2,\text{eff}}}{(1 - \zeta_{3,\text{eff}})^2} + 2 \left(\frac{\sigma_{\alpha}\sigma_{\beta}}{\sigma_{\alpha} + \sigma_{\beta}} \right)^2 \frac{(\zeta_{2,\text{eff}})^2}{(1 - \zeta_{3,\text{eff}})^2} \quad (\text{A12})$$

In the range of $1.0 < \lambda_{\alpha\beta} \leq 2.5$, the effective reduced variable $\zeta_{3,\text{eff}}$ is approximated from:

$$\zeta_{3,\text{eff}}(\lambda_{\alpha\beta}, \zeta_3) = \zeta_3 [1 + \delta(\lambda_{\alpha\beta}, \zeta_3)] \quad (\text{A13})$$

where

$$\delta(\lambda_{\alpha\beta}, \zeta_3) = \lambda_{\alpha\beta}^{5.397} (\lambda_{\alpha\beta} - 1) (1 - 0.59\zeta_3) \sum_{i=1}^6 \sum_{j=1}^6 c_{ij} \frac{\zeta_3^{i-1}}{\lambda_{\alpha\beta}^{j-1}} \quad (\text{A14})$$

and c_{ij} ’s are universal constants listed in Table A1.

In Eq. (A12), the effective reduced variable $\zeta_{2,\text{eff}}$ is calculated from:

$$\zeta_{2,\text{eff}} = \frac{\zeta_2}{\zeta_3} \zeta_{3,\text{eff}} \quad (\text{A15})$$

The term a_2^{disp} in Eq. (A5) has the same form as the term a_1^{disp} :

$$a_2^{\text{disp}} = \sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} a_{2,\alpha\beta}^{\text{disp}} \quad (\text{A16})$$

where $a_{2,\alpha\beta}^{\text{disp}}$ is related to $a_{1,\alpha\beta}^{\text{disp}}$ as follows:

$$a_{2,\alpha\beta}^{\text{disp}} = \frac{1}{2} u_{\alpha\beta} \rho_m \frac{\partial a_{1,\alpha\beta}^{\text{disp}}}{\partial \rho_m} \left(\frac{\zeta_0 (1 - \zeta_3)^4}{\zeta_0 (1 - \zeta_3)^2 + 6\zeta_1 \zeta_2 (1 - \zeta_3) + 9\zeta_3^2} \right) \quad (\text{A17})$$

The term $\tilde{a}^t$ in Eq. (A5) is calculated from:

$$\tilde{a}^t = \sum_{m=2}^5 \sum_{n=1}^2 D_{mn} \left(\frac{u}{kT} \right)^m \left(\frac{\zeta_3}{\tau} \right)^n \quad (\text{A18})$$

where D_{mn} ’s are universal constants listed in Table A2, τ is the close-packed reduced density ($=2^{1/2}\pi/6$), and u/kT is evaluated in the spirit of the van der Waals one fluid theory:

$$\frac{u}{kT} = \frac{\sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} (u_{\alpha\beta}/kT) v_{\alpha\beta}}{\sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} v_{\alpha\beta}} \quad (\text{A19})$$

where

$$v_{\alpha\beta} = \left[\frac{(v_{\alpha})^{1/3} + (v_{\beta})^{1/3}}{2} \right]^3 \quad (\text{A20})$$

Table A1The universal coefficients c_{ij} in Eq. (A14) [44].

i	j					
	1	2	3	4	5	6
1	−0.01034841243	5.012940585	−46.06908585	271.2269703	−645.5150379	605.1177799
2	0.03437151270	−45.70339147	391.8443912	−2296.265301	5430.859895	−5087.008598
3	0.04668885354	161.8370635	−1267.473745	7368.693459	−17,288.51083	16,217.30515
4	−0.28619397480	−276.0705063	1903.020452	−10,912.04277	25,296.49502	−23,885.06301
5	0.67939850140	224.7327186	−1256.163441	7025.297671	−15,911.31781	15,336.69052
6	−1.380935033	−69.71505955	242.4625593	−1,282.236283	2690.356186	−2828.288422

The molar volume of segment α (v_α) is related to the segment diameter as follows:

$$v_\alpha = \frac{\pi}{6\tau} \sigma_\alpha^3 N_{Av} \quad (A21)$$

A.3. Chain term $\tilde{a}^{chain}$

The chain term is calculated by [52]

$$\tilde{a}^{chain} = - \sum_i X_i (m_i - 1) [\ln \tilde{g}_i^{SW}(\sigma_{\alpha\beta}) - \ln \tilde{g}_{0,i}^{SW}(\sigma_{\alpha\beta})] \quad (A22)$$

and

$$\ln \tilde{g}_i^{SW}(\sigma_{\alpha\beta}) = \sum_{\beta \geq \alpha} B_{\alpha\beta,i} \ln g_{\alpha\beta}^{SW}(\sigma_{\alpha\beta}) \quad (A23)$$

where $g_{\alpha\beta}^{SW}(\sigma_{\alpha\beta})$ is the square-well radial distribution function calculated at contact, and $\tilde{g}_{0,i}^{SW}$ is $\tilde{g}_i^{SW}$ evaluated at zero density. The pair radial distribution function for a mixture of square-well segments is determined as follows:

$$g_{\alpha\beta}^{SW}(\sigma_{\alpha\beta}) = g_{\alpha\beta}^{hs}(\sigma_{\alpha\beta}) + \beta u_{\alpha\beta} g_{1,\alpha\beta}(\sigma_{\alpha\beta}) \quad (A24)$$

where $g_{\alpha\beta}^{hs}(\sigma_{\alpha\beta})$ is the pair radial distribution function for a mixture of hard sphere given by

$$g_{\alpha\beta}^{hs}(\sigma_{\alpha\beta}) = \frac{1}{1 - \zeta_3} + \frac{3\sigma_\alpha\sigma_\beta}{\sigma_\alpha + \sigma_\beta} \frac{\zeta_2}{(1 - \zeta_3)^2} + 2 \left[\frac{\sigma_\alpha\sigma_\beta}{\sigma_\alpha + \sigma_\beta} \right]^2 \frac{(\zeta_2)^2}{(1 - \zeta_3)^3} \quad (A25)$$

and $g_{1,\alpha\beta}(\sigma_{\alpha\beta})$ is the perturbation term:

$$g_{1,\alpha\beta}(\sigma_{\alpha\beta}) = \frac{1}{4u_{\alpha\beta}} \left[\frac{1}{(\pi/6)\sigma_{\alpha\beta}^3 N_{Av} \sum_i X_i m_i} \frac{\partial a_{1,\alpha\beta}}{\partial \rho} - \frac{\lambda_{\alpha\beta}}{3((\pi/6)\sigma_{\alpha\beta}^3 N_{Av} \rho \sum_i X_i m_i)} \frac{\partial a_{1,\alpha\beta}}{\partial \lambda_{\alpha\beta}} \right] \quad (A26)$$

In Eq. (A23), $B_{\alpha\beta,i}$ is the bond fraction of type $\alpha\beta$ in molecule of component i . The bond fraction of type $\alpha\alpha$ in CO_2 is equal to one since CO_2 is a homosegmented molecule. The approach for calculating $B_{\alpha\beta}$ of the cation chain for imidazolium-based ionic liquid is given in Appendix B.

Table A2The universal coefficients D_{mn} in Eq. (A18) [44].

n	m			
	2	3	4	5
1	-2.420747	-4.151326	2.501130	-0.462574
2	9.955897	-1.520369	0	0

A.4. Association term $\tilde{a}^{assoc}$

The association term is calculated by [41]

$$\tilde{a}^{assoc} = \sum_i X_i \sum_\alpha \left[\sum_{A_{\alpha i}} \left(\ln X^{A_{\alpha i}} - \frac{X^{A_{\alpha i}}}{2} \right) + \frac{n(\Gamma_{\alpha i})}{2} \right] \quad (A27)$$

where $n(\Gamma_{\alpha i})$ is the number of association sites on segment α in molecule of component i , and $X^{A_{\alpha i}}$ is the mole fraction of molecule of component i not bonded at side A of segment α calculated from:

$$X^{A_{\alpha i}} = \frac{1}{1 + \rho_n \sum_j X_j \sum_\beta \sum_{B_{\beta j}} X^{B_{\beta j}} \Delta^{A_{\alpha i} B_{\beta j}}} \quad (A28)$$

where ρ_n is the number density and $\Delta^{A_{\alpha i} B_{\beta j}}$ is the association strength between site A_α at molecule of component i and site B_β at molecule of component j given by

$$\Delta^{A_{\alpha i} B_{\beta j}} = F^{A_{\alpha i} B_{\beta j}} e^{\alpha(\rho)(u_{\alpha\beta}/kT)} g_{\alpha\beta}^{hs}(\sigma_{\alpha\beta}) (\sigma_{\alpha\beta}^3 \kappa^{A_{\alpha i} B_{\beta j}}) \quad (A29)$$

where

$$F^{A_{\alpha i} B_{\beta j}} = \exp \left(\frac{\varepsilon^{A_{\alpha i} B_{\beta j}}}{kT} \right) - 1 \quad (A30)$$

and

$$\alpha(\rho) = 1 + 0.1044\rho^* - 2.8469(\rho^*)^2 + 2.3787(\rho^*)^3 \quad (A31)$$

where ρ^* is the reduced density calculated from:

$$\rho^* = \frac{6}{\pi} \sum_\alpha \sum_\beta X_\alpha X_\beta \sigma_{\alpha\beta}^3 \quad (A32)$$

The pair distribution function in Eq. (A29) is given by the Carnahan–Starling equation for a mixture of hard spheres, i.e., Eq. (A25). The Lorentz and Berthelot combining rules are used for the size and energy parameters, i.e.:

$$\begin{cases} \sigma_{\alpha\beta} = \frac{\sigma_\alpha + \sigma_\beta}{2} \\ \sigma_\alpha = \left(\frac{\sqrt{2}}{N_{Av}} v^{\alpha 0} \right)^{1/3} \\ \varepsilon^{A_{\alpha i} B_{\beta j}} = \sqrt{\varepsilon^{A_{\alpha i}} \varepsilon^{B_{\beta j}}} \\ \kappa^{A_{\alpha i} B_{\beta j}} = \frac{1}{\sigma_{\alpha\beta}^3} \left[\frac{(\sigma_\alpha^3 \cdot \kappa^{A_{\alpha i}})^{1/3} + (\sigma_\beta^3 \cdot \kappa^{B_{\beta j}})^{1/3}}{2} \right]^3 \end{cases} \quad (A28)$$

Appendix B. The heterosegmented chain model for imidazolium-based ionic liquid

The chain term for ionic liquid is represented by the heterosegmented chain model, i.e., Eq. (A22), which in turn requires the square-well radial distribution function (rdf) calculated at contact, i.e., Eq. (A23). To calculate this term, the information of the bond

fraction of type $\alpha\beta$ in the cation chain, i.e., $B_{\alpha\beta}$, defined as [40]

$$B_{\alpha\beta} = \frac{\text{the number of bonds of type } \alpha\beta \text{ in the cation chain}}{\text{the total number of bonds in the cation chain}} = \frac{n_B^{\alpha\beta}}{n_B} \quad (\text{B1})$$

is needed. In Eq. (B1), α and β are to represent any two segments in the cation chain.

B.1. Calculation of the total number of bonds in the cation chain

The number of bonds in alkyl is calculated from [41]:

$$n_{B,\text{alkyl}} = \frac{2n - 1}{6} \quad (\text{B2})$$

where n is the number of carbons in the alkyl, while the number of bonds in imidazolium cation head (imidazole ring), $n_{B,\text{im}}$ was obtained from the fitting of experimental data [41]. Thus, the total number of bonds in the cation chain, which consists of imidazolium head and two types of alkyls, is

$$n_B = n_{B,\text{alkyl}_1} + n_{B,\text{im}} + n_{B,\text{alkyl}_2} \quad (\text{B3})$$

B.2. Calculations of the number of bonds of different types

In a cation chain, there are 5 bond types, i.e., $\alpha_1\alpha_1$, $\alpha_1\beta$, $\beta\beta$, $\alpha_2\beta$, and $\alpha_2\alpha_2$, where α_1 , α_2 , and β represent the segments of alkyl₁, alkyl₂, and cation head, respectively.

The number of bonds in an alkyl of a cation chain is the sum of the number of bonds of type $\alpha\alpha$ and the number of bonds of type $\alpha\beta$ contributed by the alkyl. The number of bonds of type $\alpha\alpha$ is the number of bonds between two alkyl segments and the number of bonds of type $\alpha\beta$ contributed by the alkyl is the number of bonds in the alkyl group that is shared with the cation head. Thus, the number of bonds of type $\alpha_1\alpha_1$ and the number of bonds of type $\alpha_2\alpha_2$ are calculated from:

$$n_B^{\alpha_1\alpha_1} = n_{B,\text{alkyl}_1} - n_{B,\text{alkyl}_1}^{\alpha_1\beta} \quad (\text{B4a})$$

$$n_B^{\alpha_2\alpha_2} = n_{B,\text{alkyl}_2} - n_{B,\text{alkyl}_2}^{\alpha_2\beta} \quad (\text{B4b})$$

The number of bonds in the cation head is the sum of the number of bonds of type $\beta\beta$, the number of bonds of type $\alpha_1\beta$ contributed by the cation head, and the number of bonds of type $\alpha_2\beta$ contributed by the cation head. The number of bonds of type $\beta\beta$ is the number of bonds between two cation head segments, the number of bonds of type $\alpha_1\beta$ contributed by the cation head is the number of bonds in the cation head that is shared with alkyl₁, and the number of bonds of type $\alpha_2\beta$ contributed by the cation head is the number of bonds in the cation head that is shared with alkyl₂. Thus, the number of bonds of type $\beta\beta$ is calculated from:

$$n_B^{\beta\beta} = n_{B,\text{im}} - n_{B,\text{im}}^{\alpha_1\beta} - n_{B,\text{im}}^{\alpha_2\beta} \quad (\text{B5})$$

The number of bonds of type $\alpha_1\beta$ is the sum of the number of bonds of type $\alpha_1\beta$ contributed by alkyl₁ and that contributed by cation head, and the number of bonds of type $\alpha_2\beta$ is the sum of the number of bonds of type $\alpha_2\beta$ contributed by alkyl₂ and that contributed by cation head. Thus:

$$n_B^{\alpha_1\beta} = n_{B,\text{alkyl}_1}^{\alpha_1\beta} + n_{B,\text{im}}^{\alpha_1\beta} \quad (\text{B6a})$$

$$n_B^{\alpha_2\beta} = n_{B,\text{alkyl}_2}^{\alpha_2\beta} + n_{B,\text{im}}^{\alpha_2\beta} \quad (\text{B6b})$$

The number of bonds of type $\alpha\beta$ contributed by an alkyl can be derived from the number of bonds contributed by a methylene group ($-\text{CH}_2-$) in an n-alkane chain because it is this methylene group that is connected to the cation head. In SAFT2, adding a methylene group to an n-alkane chain increases the number of

bonds by an increment of 1/3 [41]. That means that the number of bonds contributed by a methylene group is 1/3, and in this case only 1/6 is shared with the cation head. Thus:

$$n_{B,\text{alkyl}_1}^{\alpha_1\beta} = \frac{1}{6} \quad (\text{B7a})$$

$$n_{B,\text{alkyl}_2}^{\alpha_2\beta} = \frac{1}{6} \quad (\text{B7b})$$

The method for determining the number of bonds of type $\alpha\beta$ contributed by the cation head (imidazole ring) is somewhat arbitrary. We choose to exploit the structure of the imidazole ring to obtain a viable rule for calculating this cation head contribution. We assume that each member (N or C element) in this 5-membered ring contributes equally to the number of bonds of the cation head and we do not distinguish between single and double bonds. Since the nitrogen element is the element in the ring that is connected to the alkyl and this element also shares its bonds with two other carbon elements of the cation head, only one-third of the number of bonds contributed by nitrogen element is shared with alkyl. Thus:

$$n_{B,\text{im}}^{\alpha_1\beta} = \frac{1}{3} \left(\frac{n_{B,\text{im}}}{5} \right) = \frac{n_{B,\text{im}}}{15} \quad (\text{B8a})$$

$$n_{B,\text{im}}^{\alpha_2\beta} = \frac{1}{3} \left(\frac{n_{B,\text{im}}}{5} \right) = \frac{n_{B,\text{im}}}{15} \quad (\text{B8b})$$

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