Methodology of non-equilibrium thermodynamics for kinetics research of CO₂ capture by ionic liquids

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In this paper, the methodology of non-equilibrium thermodynamics is introduced for kinetics research of CO₂ capture by ionic liquids, and the following three key scientific problems are proposed to apply the methodology in kinetics research of CO₂ capture by ionic liquids: reliable thermodynamic models, interfacial transport rate description and accurate experimental flux. The obtaining of accurate experimental flux requires reliable experimental kinetics data and the effective transport area in the CO₂ capture process by ionic liquids. Research advances in the three key scientific problems are reviewed systematically and further work is analyzed. Finally, perspectives of non-equilibrium thermodynamic research of the kinetics of CO₂ capture by ionic liquids are proposed.

ionic liquids, CO₂ capture, non-equilibrium thermodynamics, interfacial transport rate, nanobubble, statistical rate theory

1 Introduction

The combustion of fossil fuels such as natural gas, petroleum, and coal leads to a great increase of the CO₂ concentration in the atmosphere. As CO₂ is considered to be one of the most important greenhouse gases (responsible for about 64% of the enhanced “greenhouse effect” [1]), the capture and sequestration of CO₂ has become a hot issue of worldwide concern [1–3]. It is reported that the capture of CO₂ alone will increase the energy requirements of a plant by 25%–40% [3]. Therefore, many scientists all over the world are focusing on the investigations of the environment-friendly capture technology with higher efficiency and lower energy consumption compared with the current technologies [3–9].

Amine-based chemical absorption technology is currently a mature, effective and applied way to separate CO₂ from flue gases, natural gases, and syngas [10–14]. However, due to the corrosion, volatility, toxicity of the amines, and their high regeneration energy requirement in the applications, in

recent years, scientists all over the world have designed and synthesized many ionic liquids (ILs) as absorbents to absorb and separate CO₂ from the gas mixtures [5–9, 15–30]. The IL-based CO₂ capture technology is considered to be a promising and competitive way to separate CO₂ because of its advantages of non-volatility, recycling, environment-friendliness, functionality, and high efficiency of CO₂ capture [9]. Although ionic liquids show a promising prospect for CO₂ capture, their industrialization and commercialization still face difficulties due to their high viscosity and high price [9, 30]. To develop the process intensification technologies for IL-based CO₂ capture, it is necessary to investigate the kinetics process of CO₂ capture and to study the effects of different operation parameters on the rate of CO₂ capture.

2 Non-equilibrium thermodynamic investigation of CO₂ capture by ionic liquids

2.1 Model description of CO₂ absorption by ionic liquids

Based on our previous work of linear non-equilibrium

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thermodynamic investigations on the dissolution and crystallization kinetics of potassium inorganic compounds [31–33], in this paper, the kinetic process of CO₂ absorption by ionic liquids is assumed to comprise two steps: surface reaction and diffusion, which is shown in Figure 1. As shown in Figure 1, when CO₂ in the vapor phase and the ionic liquids are in contact, for the chemical absorption process of CO₂ by ionic liquids in the first step, the chemical reaction of CO₂ with ionic liquids takes place, which is called the surface reaction layer; for the physical absorption process of CO₂ by ionic liquids in the first step, CO₂ in the vapor phase will be transferred into the ionic liquid phase, which could also be called the assumed “surface reaction layer”. For the surface reaction layer, the chemical potential gradient of CO₂ between CO₂ gas and CO₂ at the vapor-liquid interface is the driving force of the surface reaction. In the second step, CO₂ in the ionic liquid phase will diffuse from the vapor-liquid interface into the bulk solutions, which is called the diffusion layer. In the diffusion layer, the chemical potential gradient of CO₂ between the vapor-liquid interface and the bulk phase is the driving force for the diffusion in solutions. The reciprocals of the surface reaction rate constant and the diffusion rate constant are their respective resistances. Therefore, in order to describe the rate of the CO₂ capture process, it is important to investigate the transport rate of CO₂ at the vapor-liquid interface. Analysis of the resistances of the surface reaction layer and the diffusion layer in the kinetic process of CO₂ capture by ionic liquids and investigation of the effects of different operation parameters on the respective resistances might provide useful information for the analysis of the simple and controllable parameters of the process intensification for IL-based CO₂ capture.

2.2 Non-equilibrium thermodynamic model of CO₂ absorption by ionic liquids

Non-equilibrium thermodynamic principles [33–35] mainly focus on the entropy production of the systems due to the irreversible process. When the system is close to the equilibrium state (or the deviation from the equilibrium state is not far), the generalized flux is linearly related to the gen-

Figure 1 Schematic diagram of CO₂ absorption process by ionic liquids.

eral driving force [33–35], namely

$$J_j = \sum_k L_{jk} X_k \quad (1)$$

In eq. (1), L_{jk} is called the phenomenological coefficient.

The non-equilibrium thermodynamic model of CO₂ absorption kinetics by ionic liquids could be investigated on the basis of the schematic diagram of CO₂ absorption kinetics process by ionic liquids shown in Figure 1 and our previous linear non-equilibrium thermodynamic investigations on the dissolution and crystallization kinetics of potassium inorganic compounds [31–33]. In this paper, the surface reaction rate and diffusion rate will be described using the linear non-equilibrium thermodynamic theory.

The surface reaction rate is described by eq. (2).

$$J = K_s (f_s - f_i) \quad (2)$$

The diffusion rate is described by eq. (3).

$$J = K_d (f_i - f_b) \quad (3)$$

In eqs. (2) and (3), J is the CO₂ absorption rate (flux) by ionic liquids in mol m⁻² s⁻¹ or kg m⁻² s⁻¹; K_s and K_d represent the surface reaction rate constant and diffusion rate constant, respectively, in m s⁻¹; f_s , f_i and f_b represent the fugacities of CO₂ in ionic liquid at equilibrium, at the vapor-liquid interface and the bulk phase of the ionic liquids, respectively.

2.3 Key scientific problems of non-equilibrium thermodynamic investigations on CO₂ absorption kinetics by ionic liquids

In this paper, three key scientific problems of non-equilibrium thermodynamic investigations on CO₂ absorption kinetics by ionic liquids are proposed on the basis of the non-equilibrium thermodynamic model of CO₂ absorption kinetics by ionic liquids as described in Section 2.2 and our previous linear non-equilibrium thermodynamic investigations on the dissolution and crystallization kinetics of potassium inorganic compounds [31–33]. These problems are shown as follows.

(1) Reliable solubility of CO₂ in ionic liquids and reliable thermodynamic models for describing the thermodynamic properties of systems;

(2) Accurate experimental data of CO₂ absorption rate (flux) by ionic liquids;

(3) Transport rate of CO₂ in ionic liquid at the vapor-liquid interface in the CO₂ absorption process by ionic liquids.

3 Advances in non-equilibrium thermodynamic investigation of CO₂ capture by ionic liquids

According to the three key scientific problems of non-equilibrium thermodynamic investigations on CO₂ absorption kinetics by ionic liquids as analyzed in Section 2.3, in this paper, research advances in the non-equilibrium thermody-

namic investigation of CO₂ capture by ionic liquids will be reviewed from the three aspects, and further research will be proposed.

3.1 Solubility of CO₂ in ionic liquids

3.1.1 Experimental data of phase equilibrium for CO₂-ionic liquid systems

On one hand, reliable experimental data of phase equilibrium for CO₂-ionic liquid systems could provide important

fundamental data for the analysis of the CO₂ capture capacity by ionic liquids. On the other hand, reliable experimental data of phase equilibrium for CO₂-ionic liquid systems are important basis for obtaining the parameters of thermodynamic models and verifying the reliability of the models. In this section, the experimental data of phase equilibrium for CO₂-ionic liquid systems are summarized and listed in Table 1.

As shown in Table 1, a large number of experimental investigations on CO₂ solubility in ionic liquids have been

Table 1 Experimental investigations on CO₂ solubility in ionic liquids

Ionic liquids	Temperature & pressure range	Ref.	Year
[bmim][PF ₆], [C ₈ mim][PF ₆], [C ₈ mim][BF ₄], [bmim][NO ₃], [emim][EtSO ₄], [N-bupy][BF ₄]	high pressure	Blanchard <i>et al.</i> [16]	2001
[bmim][PF ₆]	283.15, 298.15, 323.15 K, gas pressures up to 1.3 MPa	Anthony <i>et al.</i> [36]	2002
[bmim][PF ₆]	293–395 K, pressures up to 9.7 MPa	Kamps <i>et al.</i> [37]	2003
[bmim][BF ₄]	303–343 K, pressures close to atmospheric pressure	Husson-Borg <i>et al.</i> [38]	2003
[bmim][PF ₆]	313.15, 323.15, 333.15 K, pressures up to 12.5 MPa	Liu <i>et al.</i> [39]	2003
[bmim][PF ₆], [emim][Tf ₂ N], [emim][CF ₃ SO ₃], [emim][dca], [thtdp][Cl]	303.15 K, low partial pressures (< 1 atm)	Scovazzo <i>et al.</i> [40]	2004
[emim][PF ₆]	308.14–366.03 K, 1.49–97.10 MPa	Shariati and Peters [41]	2004
[bmim][PF ₆], [bmim][PF ₆], [bmim][BF ₄], [bmim][BF ₄], [emim][Tf ₂ N], [emim][Tf ₂ N]	283.15 K, 298.15 K, 323.15 K	Cadena <i>et al.</i> [42]	2004
[bmim][BF ₄], [bmim][TfO], [bmim][methide], [bmim][DCA], [bmim][PF ₆], [bmim][NO ₃], [bmim][Tf ₂ N], [hmim][Tf ₂ N], [omim][Tf ₂ N], [hmim][Tf ₂ N]	298.15 K, 313.15 K, 333.15 K, pressures up to 15 MPa	Aki <i>et al.</i> [43]	2004
[hmim][PF ₆]	298.31–363.58 K, 0.64–94.60 MPa	Shariati and Peters [44]	2004
[bmim][PF ₆], [C ₆ mim][PF ₆], [emim][BF ₄], [C ₆ mim][BF ₄], [emim][Tf ₂ N], [C ₆ mim][Tf ₂ N]	298.15 K, pressures up to 1 MPa	Kim <i>et al.</i> [45]	2005
[bmim][BF ₄]	278.47–368.22 K	Kroon <i>et al.</i> [46]	2005
TMGL, [bmim][PF ₆]	297–328 K, 0–11 MPa	Zhang <i>et al.</i> [19]	2005
[P _{6,6,6,14}][C ₁₂ H ₂₅ PhSO ₃], [P _{6,6,6,14}][MeSO ₃]	305–325 K, 4–9 MPa	Zhang <i>et al.</i> [20]	2005
[bmim][PF ₆], [bmim][BF ₄]	283.15, 298.15, 323.15, 348.15 K, pressures below 2 MPa	Shiflett and Yokozeki [47]	2005
[bmim][BF ₄], [bmim][Tf ₂ N], [bmim][PF ₆]	283.15, 298.15, 323.15 K, gas pressures up to 1.3 MPa	Anthony <i>et al.</i> [48]	2005
[desmim][TfO], [emim][Tf ₂ N], [emim][BETI], [bmim][PF ₆], [emim][TfO], [thtdp][Cl]	303.15 K	Morgan <i>et al.</i> [49]	2005
[hmim][BF ₄]	293.18–368.16 K	Costantini <i>et al.</i> [50]	2005
[bmim][PF ₆]	293.29–363.54 K, 0.59–73.50 MPa	Shariati <i>et al.</i> [51]	2005
[bmim][BF ₄], [hmim][BF ₄], [omim][BF ₄]	305–325 K, 1–9 MPa	Chen <i>et al.</i> [23]	2006
[emim][Tf ₂ N]	303.15–343 K	Camper <i>et al.</i> [52]	2006
[hmim][Tf ₂ N]	293.15–413.2 K, pressures up to 10 MPa	Kumelan <i>et al.</i> [53]	2006
[omim][BF ₄]	303–363 K, 0.1–100 MPa	Gutkowski <i>et al.</i> [54]	2006
[bmim][Tf ₂ N]	298.15–343.15 K, pressures up to 30 MPa	Oh and Lee [55]	2006
[bmim][PF ₆]	283–343 K, pressures close to atmospheric pressure	Jacquemin <i>et al.</i> [56]	2006
[bmim][PF ₆], [bmim][BF ₄]	283.15–348.15 K, pressures below 2 MPa	Shiflett and Yokozeki [57]	2006
[bmim][Tf ₂ N]	280–340 K	Lee and Outcalt [58]	2006

(To be continued on the next page)

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Ionic liquids	Temperature & pressure range	Ref.	Year
[bmim][CH ₃ SO ₃]	293.2–413.1 K, pressures up to 10 MPa	Kumelan <i>et al.</i> [59]	2006
[bmim][PF ₆] HEF, HEA, HEL, THEAA, THEAL, HEAF, HEAA, HEAL	293–395 K, pressures up to 9.7 MPa 303–323 K, 0–11 MPa	Yuan <i>et al.</i> [60]	2007
[C ₄ mim][Tf ₂ N], [C ₇ mim][Tf ₂ N], [C ₁₀ mim][Tf ₂ N], [P ₁ mim][Tf ₂ N], [P ₂ mim][Tf ₂ N], [P ₃ mim][Tf ₂ N] P[VBtMA][BF ₄], P[VBMi][BF ₄]	313.15 K, low pressures (1 atm) 298.15, 323.15, 348.15 K, pressures up to 18 MPa	Bara <i>et al.</i> [61] Blasig <i>et al.</i> [62]	2007 2007
[hmim][Tf ₂ N]	282, 297, 323, 348 K, pressures up to about 2 MPa	Shiflett and Yokozeki [63]	2007
[emim][Tf ₂ N] [P ₍₁₄₎₆₆₆ ⁺][Cl [−]], [P ₍₁₄₎₆₆₆ ⁺][DCA [−]], [P ₍₁₄₎₆₆₆ ⁺][Tf ₂ N [−]], [P ₂₄₄₄ ⁺][DEP [−]], [P ₍₁₄₎₄₄₄ ⁺][DBS [−]]	310–450 K, 0–15 MPa 303.15 K	Schilderman <i>et al.</i> [64] Ferguson and Scovazzo [65]	2007 2007
[bmim][Tf ₂ N], [pmmim][Tf ₂ N], [bmpy][Tf ₂ N], [perfluoro- hmim][Tf ₂ N], [bmim][BF ₄] [N ₄₁₁₁][Ntf ₂], [C ₄ mim][Ntf ₂], [C ₂ mim][Ntf ₂]	283–323 K 283–343 K, pressures close to atmospheric pressure	Hou and Baltus [66] Jacquemin <i>et al.</i> [67]	2007 2007
[C ₆ mim][NTf ₂]	283–343 K, pressures close to atmospheric pressure	Costa Gomes [68]	2007
[C ₆ mim][Tf ₂ N] [hmim][Tf ₂ N], [hmmim][Tf ₂ N], [bmim][TFA], [bmim][C ₇ F ₁₅ CO ₂], [b ₂ -Nic][Tf ₂ N], [hmpy][Tf ₂ N], [hmim][eFAP], [hmim][pFAP], [p ₃ mim][bFAP], [N ₄₄₄₄][doc], [C ₆ H ₄ F ₉ mim][Tf ₂ N], [C ₈ H ₄ F ₁₃ mim][Tf ₂ N], Ecoeng 500, Ecoeng 41 M, [hmim][SAC], [hmim][ACE], [Et ₃ NBH ₂ mim][Tf ₂ N], [choline][Tf ₂ N], [N ₄₁₁₁][Tf ₂ N], [hmim][PF ₆], [bmim][Tf ₂ N], [bmim][methide] [hmim][Tf ₂ N]	298.15 K, pressure up to 1 MPa 283.15 K, 298.15 K, 333.15 K 333 K, 0.3–2 MPa	Kim <i>et al.</i> [69] Muldoon <i>et al.</i> [70] Shi <i>et al.</i> [71]	2007 2007 2008
[bmim][PF ₆], [emim][BF ₄]	303.2–343.2 K, pressures below 5 MPa	Soriano <i>et al.</i> [72]	2008
[C ₂ mim][Tf ₂ N], [C ₄ mim][Tf ₂ N], [C ₆ mim][Tf ₂ N], [C ₈ mim][Tf ₂ N]	298.15–343.15 K, pressures up to 45 MPa	Shin <i>et al.</i> [73]	2008
TEGOIL K5	Temperatures up to 500 K, pressures up to 3 MPa	Heintz <i>et al.</i> [74]	2009
[bmim][PF ₆]	313 K, 15 MPa	Andanson <i>et al.</i> [75]	2009
[HMIm][Tf ₂ N]	343.15 K	Ahosseini <i>et al.</i> [76]	2009
[emim][Tf ₂ N], [bmim][Tf ₂ N]		Raeissi and Peters [77]	2009
[C ₂ mim][Tf ₂ N], [C ₅ mim][Tf ₂ N]	Temperatures up to 363 K, pressures up to 50 MPa	Carvalho <i>et al.</i> [78]	2009
[bmim][Tf ₂ N]	310–450 K, 0.5–14.0 MPa	Raeissi and Peters [79]	2009
[C ₄ mim][DCA], [C ₄ mim][Tf ₂ N]	Temperatures up to 363 K, pressures up to 74 MPa	Carvalho <i>et al.</i> [80]	2009
[emim][Tf ₂ N], [emim][BETI], [emim][TfO], [emim][TfA], [hmim][Tf ₂ N], [hmim][BF ₄], [Omim][BF ₄], [Bmpy][BF ₄] [hemim][BF ₄]	283.15 K, 298.15 K, 313.15 K, low pressures 303.15–353.15 K, pressures up to 1.1 MPa	Moganty and Baltus [81] Shokouhi <i>et al.</i> [82]	2010 2010
[emim][EtSO ₄]	303.15–353.15 K, pressures up to 1.6 MPa	Jalili <i>et al.</i> [83]	2010
[bmim][PF ₆]		Shiflett and Yokozeki [84]	2010
[C ₁₀ mim][Tf ₂ N]	313.15 K, 2.00–14.40 MPa	Bogel-Lukasik <i>et al.</i> [85]	2010
[DMFH][Tf ₂ N]		Kodama <i>et al.</i> [86]	2010
[bmpy][Tf ₂ N]	293.1–413.2 K, pressures up to 10.8 MPa	Kumelan <i>et al.</i> [87]	2010
[emim][BF ₄]	298.2 and 313.2 K, pressures up to 8.0 MPa	Lei <i>et al.</i> [88]	2010
[bmim][BF ₄], [bmim][SCN], [dmim][MP], [(ETO) ₂ IM][Tf ₂ N]	Temperatures up to 373 K, pressures up to 30 MPa	Revelli <i>et al.</i> [89]	2010
[emim][Tf ₂ N], [hmim][Tf ₂ N], [dmim][Tf ₂ N]	298.15 K, 323.15 K, 343.15 K, pressures up to 25 MPa	Ren <i>et al.</i> [90]	2010
[MDEA][Cl]	313.15–333.15 K, 1.22–8.62 MPa	Zhao <i>et al.</i> [30]	2011
[emim][BF ₄]	293.2–323.2 K	Hwang <i>et al.</i> [91]	2011
[hmim][BF ₄]	303.2–328.2 K		

performed. In this paper, in order to study the consistency of the experimental data from different sources, and as the experimental investigations on the phase equilibrium of CO₂-[bmim][PF₆] system are more extensive, CO₂-[bmim][PF₆] system will be selected as a model system to compare and analyze the experimental CO₂ solubility data in [bmim][PF₆] at different temperatures and pressures and from different literature sources. The results are shown in Figure 2.

Figure 2 describes the experimental CO₂ solubility data in [bmim][PF₆] at different temperatures and pressures and from different literature sources. As shown in Figure 2, under all the investigated temperatures, when the temperature is constant, the solubilities of CO₂ in [bmim][PF₆] increase with the increasing pressures. As shown in Figure 2(a), (b), (c), at the temperatures of 283, 293 and 298 K, the experimental CO₂ solubility data in [bmim][PF₆] from different literature sources agree with each other. As shown in Figure 2(d), (e), (f), at the temperatures of 313, 323 and 333 K, when the pressure is below 2 MPa, the experimental CO₂ solubility data in [bmim][PF₆] from different literature sources agree with each other, while at the pressures higher than 2 MPa, apparent discrepancies could be observed for the experimental CO₂ solubility data in [bmim][PF₆] from different literature sources. As shown in Figure 2(g), (h), (i), (j), when the temperatures are increased to 348, 353, 373 and 393 K, there are less experimental investigations of the CO₂ solubility in [bmim][PF₆], and the available investigations show that the experimental CO₂ solubility data in [bmim][PF₆] from different literature sources agree with each other.

3.1.2 Theoretical models

As analyzed in Section 2.3, it is important to develop reliable thermodynamic models for describing the thermodynamic properties of CO₂-ionic liquid systems, which is one of the key scientific problems of non-equilibrium thermodynamic investigation on CO₂ absorption kinetics by ionic liquids. In recent years, different theoretical approaches, correlation models and equations of state (EoS) have been developed to describe the thermodynamic properties of CO₂-ionic liquid systems. Vega *et al.* [92] presented a systematic review of different theoretical approaches that have been applied to describe the thermodynamic behaviors of ionic liquids and the solubility of representative compounds (CO₂, H₂, H₂O, BF₃) in them. In their review, the most recent research advances in the theoretical approaches and the advantages and disadvantages of the respective thermodynamic models were analyzed in detail, and the advantages of the models based on statistical mechanics versus classical ones were emphasized. Moreover, the research framework of Soft-SAFT was also presented. On the basis of their review, this section presents a brief introduction to the available theoretical models for CO₂-ionic liquid systems in recent years, which are summarized in Table 2.

As shown in Table 2, Scovazzo *et al.* [40] predicted CO₂

solubility in room-temperature ionic liquids [emim][Tf₂N] and [bmim][BF₄] at temperatures of 298.15 and 310.15 K using the regular solution theory and produced reasonable estimates. Moganty and Baltus [81] interpreted the low pressure solubility of CO₂ in eight commercially available room-temperature ionic liquids, [emim][Tf₂N], [emim][BETI], [emim][TfO], [emim][TfA], [hmim][Tf₂N], [hmim][BF₄], [Omim][BF₄], and [Bmpy][BF₄], at temperatures of 283.15, 298.15 and 313.15 K using the regular solution theory. Shiflett and Yokozeki [47] successfully correlated the experimental CO₂ solubility data in the ionic liquids at temperatures of 283.15, 298.15, 323.15 and 348.15 K and pressures below 2 MPa using a generic RK type cubic EoS, and they predicted the phase behaviors of CO₂ and ionic liquid mixtures as well as Henry's law constants and the volume change of solutions. Shiflett and Yokozeki [63] successfully correlated the experimental CO₂ solubility data in the ionic liquid [hmim][Tf₂N] at temperatures of 282, 297, 323, and 348 K and pressures up to about 2 MPa using a generic RK type cubic EoS. In order to understand the separation of CO₂ and H₂S using room-temperature ionic liquid [bmim][PF₆], Shiflett and Yokozeki [84] developed a ternary equation of state to describe the phase behaviors of the CO₂/H₂S/[bmim][PF₆] system based on a generic RK EoS combined with the empirical interaction parameters of each binary system. The interaction parameters in the model were determined by regressing the previously measured vapor-liquid equilibrium data for CO₂/[bmim][PF₆] system and reported data for H₂S/[bmim][PF₆] and CO₂/H₂S systems in the literature. Yuan *et al.* [60] successfully correlated the experimental CO₂ solubility data in eight hydroxyl ammonium ionic liquids, HEF, HEA, HEL, THEAA, THEAL, HEAF, HEAA, HEAL, at temperatures ranging from 303 to 323 K and pressures ranging from 0 to 11 MPa using Krichevsky-Kasarnovsky equation. Shokouhi *et al.* [82] and Jalili *et al.* [83] correlated the experimental solubilities of CO₂ and H₂S in the ionic liquids [hemim][BF₄] and [emim][EtSO₄] at temperatures ranging from 303.15 to 353.15 K and pressures up to 1.1 MPa and temperatures ranging from 303.15 to 353.15 K and pressures up to 1.6 MPa using the Krichevsky-Kasarnovsky equation. Bogel-Lukasik *et al.* [85] described the phase behaviors of the ternary systems containing CO₂, 1-propanol, and ionic liquids [C₂mim][Tf₂N] or [C₂mim][TfO] or [C₁₀mim][Tf₂N] using the Peng-Robinson and Soave-Redlich-Kwong equations of state with the Mathias-Klotz-Prausnitz mixing rule. Álvarez and Aznar [96] correlated the vapor-liquid phase equilibrium data reported for binary systems including CO₂ and ionic liquids with the thermodynamic models. The Peng-Robinson EoS coupled with the van der Waals and Wong-Sandler mixing rules was used to calculate the fugacity coefficients of the systems. The UNIQUAC and NRTL models were used to calculate the excess Gibbs free energy in the Wong-Sandler mixing rule.

Molecule-based approaches have attracted increasingly

Figure 2 Experimental CO₂ solubility data in [bmim][PF₆] at different temperatures and pressures and from different literature sources.

Table 2 Thermodynamic models for CO₂-ionic liquid systems

Thermodynamic models		Ionic liquids	Thermodynamic properties	Temperature & pressure range	Ref.	Year
Regular Theory	Solution	[emim][Tf ₂ N]	solubility	298.15 K, 310.15 K	Scovazzo <i>et al.</i> [40]	2004
		[bmim][BF ₄], [emim][Tf ₂ N], [emim][BETI], [emim][TfO], [emim][TfA], [hmim][Tf ₂ N], [hmim][BF ₄], [Omim][BF ₄], [Bmip][BF ₄]	solubility	283.15 K, 298.15 K, 313.15 K, low pressures	Moganty and Baltus [81]	2010
Redlich-Kwong EoS		[bmim][PF ₆], [bmim][BF ₄]	solubility, phase behaviors of CO ₂ and ionic liquid mixtures	283.15, 298.15, 323.15, 348.15 K, pressures below 2 MPa	Shiflett and Yokozeki [47]	2005
		[hmim][Tf ₂ N]	solubility	282 K, 297 K, 323 K, 348 K, pressures up to about 2 MPa	Shiflett and Yokozeki [63]	2007
		[bmim][PF ₆]	solubility, phase behaviors of mixtures		Shiflett and Yokozeki [84]	2010
SWCF-EoS		[C _n mim][BF ₄], [C _n mim][PF ₆] and [C _n mim][Tf ₂ N]	solubility, <i>pVT</i> behavior of ionic liquids	293–393 K, 0.1–15.2 MPa	Wang <i>et al.</i> [93]	2006
tPC-PSAFT EoS		[emim][PF ₆], [bmim][PF ₆], [hmim][PF ₆], [omim][PF ₆], [emim][BF ₄], [bmim][BF ₄], [hmim][BF ₄], [omim][BF ₄]	solubility	0–100 MPa	Kroon <i>et al.</i> [94]	2006
Soft-SAFT EoS		[C _n mim][BF ₄] and [C _n mim][PF ₆]	solubility	283 K, 298 K, 323 K, 330 K, 348 K, up to high pressures	Andreu and Vega [95]	2007
Krichevsky-Kasarnovsky EoS		HEF, HEA, HEL, THEAA, THEAL, HEAF, HEAA, HEAL, [hemim][BF ₄]	solubility, Henry's constants	303–323 K, 0–11 MPa	Yuan <i>et al.</i> [60]	2007
			solubility, partial molar thermodynamic functions of solution	303.15–353.15 K, pressures up to 1.1 MPa	Shokouhi <i>et al.</i> [82]	2010
		[emim][EtSO ₄]	solubility, partial molar thermodynamic functions of solution	303.15–353.15 K, pressures up to 1.6 MPa	Jalili <i>et al.</i> [83]	2010
Peng-Robinson EoS Soave-Redlich-Kwong EoS		[C ₂ mim][Tf ₂ N], [C ₂ mim][TfO] and [C ₁₀ mim][Tf ₂ N]	phase behaviors of mixtures	313.15 K, pressures from 9 to 12 MPa	Bogel-Lukasik <i>et al.</i> [85]	2010
Peng-Robinson EoS UNIQUAC and NRTL model		[bmim][NO ₃], [bmim][PF ₆], [omim][BF ₄], [omim][PF ₆], [emim][EtSO ₄], [emim][PF ₆], [hmim][PF ₆], [N-bupy][BF ₄]	vapor-liquid phase equilibrium	308–359 K, 1–958 atm	Álvarez and Aznar [96]	2008
Hetero-SAFT EoS		[C ₂ mim][Tf ₂ N], [C ₄ mim][Tf ₂ N], [C ₆ mim][Tf ₂ N], [C ₈ mim][Tf ₂ N], [C ₂ mim][BF ₄], [C ₄ mim][BF ₄], [C ₆ mim][BF ₄], [C ₈ mim][BF ₄], [C ₄ mim][PF ₆], [C ₆ mim][PF ₆], [C ₈ mim][PF ₆]	solubility	283–415 K, pressures up to 20 MPa	Ji and Adidharma [97]	2010

more interest of scientists and engineers all over the world. Recently, research advances have been achieved in the description of the thermodynamic properties of CO₂-ionic liquid systems with the molecular thermodynamic models. Wang *et al.* [93] described the *pVT* behavior of ionic liquids and the solubilities of representative gases in the ionic liquids by extending the molecular thermodynamic model (the square-well chain fluids (SWCF) EoS) developed by their group. Their research results showed that the SWCF EoS could be used to describe the CO₂ solubility in ionic liquids with only one temperature-independent adjustable interaction parameter, and the accuracy of the correlation could be

further improved by using two temperature-independent adjustable interaction parameters. Kroon *et al.* [94] developed an equation of state based on the truncated perturbed chain polar statistical associating fluid theory (tPC-PSAFT) EoS and described the CO₂ solubility in various imidazolium-based ionic liquids at pressures from 0 to 100 MPa. Andreu and Vega [95] described the CO₂ solubility in ionic liquids [C_nmim][BF₄] and [C_nmim][PF₆] with the soft-SAFT EoS, and the results show that their model is able to capture the CO₂ solubility in ionic liquids in quantitative agreement with experimental data. Ji and Adidharma [97] presented the CO₂ solubility in the imidazolium ionic liq-

uids [C₂mim][Tf₂N], [C₄mim][Tf₂N], [C₆mim][Tf₂N], [C₈mim][Tf₂N], [C₂mim][BF₄], [C₄mim][BF₄], [C₆mim][BF₄], [C₈mim][BF₄], [C₄mim][PF₆], [C₆mim][PF₆] and [C₈mim][PF₆] at temperatures from 283 to 415 K and pressures up to 20 MPa with the heterosegmented statistical associating fluid theory (hetero-SAFT) EoS, and the results agreed with the experimental data.

In this paper, the brief review of the available theoretical models for CO₂-ionic liquid systems in recent years shows that the classical equations of state have been used for correlation, and the molecular thermodynamic models such as SAFT EoS and SWCF EoS have been used to describe the phase behaviors of CO₂-ionic liquid systems and show excellent potential for applications in engineering. However, more research is needed concerning the thermodynamic properties of more CO₂-ionic liquid systems using the molecule-based approaches.

3.1.3 Molecular simulation

With the development of information science, molecular simulation shows increasingly more advantages compared with the experiments. In recent years, increasingly more scientists and engineers have investigated the phase equilibrium of CO₂-ionic liquid systems with molecular simulation. Shah and Maginn [98] investigated the volumetric properties such as density, isothermal compressibility and volume expansivity of the ionic liquid [bmim][PF₆] at a temperature range from 298 to 343 K by the Monte Carlo simulation with a modified united atom force field, and the results were in reasonable agreement with the available experimental data. Moreover, in their work, Henry's constants and the infinite dilution enthalpy and entropy of absorption for CO₂ in the ionic liquid were also computed and the predicted CO₂ solubility in the IL was slightly greater than the experimental data, which might be due to an overestimation of the interaction strength between CO₂ and the IL in the simulation. Urukova *et al.* [99] predicted the solubility of CO₂, CO and H₂ in the ionic liquid [bmim][PF₆] at a temperature range from 293 to 393 K and pressures up to 9 MPa by Gibbs ensemble Monte Carlo simulations (*NpT*-GEMC). The simulation results for the solubility of H₂ agreed within their statistical uncertainty with the experimental data, while the predicted solubilities for CO₂ and CO in the IL showed larger deviations. Shah and Maginn [100] investigated the solubility of CO₂, H₂O, C₂H₆, C₂H₄, CH₄, O₂ and N₂ in the ionic liquid [bmim][PF₆] by the test particle insertion and expanded ensemble Monte Carlo simulations. The partial molar enthalpy and partial molar entropy of solvation were computed for CO₂, H₂O and O₂. The results showed higher solubilities than the available experimental data for most of the investigated gases. Wang *et al.* [101] investigated the solubility of CO₂ and SO₂ in the ionic liquid TMGL by the molecular dynamics simulations, and their simulation results well explained the selectivity of the TMGL toward SO₂ and CO₂. Shi and Maginn [102] investigated the solu-

bility of CO₂ and H₂O in the ionic liquid [hmim][Tf₂N] using atomistic Monte Carlo simulations and the computed results were in quantitative agreement with the available experimental data. Shi *et al.* [71] investigated the solubility of pure and mixed CO₂, H₂ and Ar gases absorbed in the ionic liquid [hmim][Tf₂N] using the classical molecular dynamics and Monte Carlo simulations. The results show the strongest interaction for CO₂ with the IL, about six times larger than that of H₂ with the IL and two times larger than that between Ar and the IL, which is consistent with a decreasing solubility from CO₂ to Ar and then to H₂. However, in their study the simulation results do not agree with the experimental data at high temperatures. Zhang *et al.* [103] investigated CO₂ absorption isotherms in the ionic liquid [hmim][FEP] at temperatures of 298.2 and 323.2 K and pressures up to 2 MPa using the continuous fractional component Monte Carlo (CFC MC) method. The simulated isotherms agreed with the experimental results in the trend but overestimate the CO₂ solubility by about 20%. The energetic analysis shows that the van der Waals interactions between CO₂ and the investigated ILs are stronger than the electrostatic interactions. Kerlé *et al.* [104] investigated the CO₂ solubility in the ionic liquids [C_{*n*}mim][NTf₂] (*n* = 2, 4, 6, 8) using the molecular dynamics simulations.

The above brief introduction shows that significant research progress has been made for investigations on the phase equilibrium of CO₂-ionic liquids using molecular simulations. However, apparent discrepancies between the simulated results and the experimental data are observed due to the limitations of the force field.

3.2 Experimental data of CO₂ absorption rate (flux) by ionic liquids

3.2.1 Experimental investigations on CO₂ absorption kinetics by ionic liquids

Compared with experimental investigations on CO₂ solubility in ionic liquids, less experimental investigations on CO₂ absorption kinetics by ionic liquids have been reported recently. The latter shows that a large number of experimental kinetics studies focus on the investigations of the CO₂ diffusion coefficient in ionic liquids, while the experimental kinetics data that could be used to analyze the rate-controlling step of CO₂ absorption by ionic liquids using the linear non-equilibrium thermodynamic modeling proposed in this paper have rarely been reported. Shiflett and Yokozeki [47] measured the CO₂ absorption kinetics in ionic liquids [bmim][PF₆] and [bmim][BF₄] using the gravimetric microbalance method at temperatures of 283.15, 298.15, 323.15, and 348.15 K and pressures below 2 MPa. From the time-dependent absorption data, binary diffusion coefficients of CO₂ in the ionic liquids were determined using a simple diffusion model. Morgan *et al.* [49] measured the diffusivity of CO₂, ethylene, propylene, 1-butene, and 1,3-butadiene in five imidazolium-based ionic liquids, [des-

mim][TfO], [emim][Tf₂N], [bmim][BETI], [bmim][PF₆], and [emim][TfO], and one phosphonium-based ionic liquid [thtdp][Cl] using a lag-time technique. Camper *et al.* [52] measured the absorption kinetics data of the representative gases CO₂, ethane, ethene, propane, and propene in the room-temperature ionic liquid [emim][Tf₂N], and determined the diffusion coefficients of the gases in the RTILs using a semi-infinite volume approach. Ferguson and Scovazzo [65] measured the diffusivity of the gases CO₂, ethylene, propylene, butene, and 1,3-butadiene in five phosphonium-based ionic liquids, [P₍₁₄₎₆₆₆⁺][Cl⁻], [P₍₁₄₎₆₆₆⁺][DCA⁻], [P₍₁₄₎₆₆₆⁺][Tf₂N⁻], [P₂₄₄₄⁺][DEP⁻], and [P₍₁₄₎₄₄₄⁺][DBS⁻], at 303.15 K using a lag-time technique. From their research results, the diffusivities of the representative gases in the phosphonium-based ILs are of the same order of magnitude as that in the imidazolium-based ILs, which shows that the phosphonium-based ILs can be considered as low-cost alternatives to the imidazolium-based ILs for reaction media or separation agents. Hou and Baltus [66] measured the CO₂ diffusivity in the ionic liquids [bmim][Tf₂N], [pmmim][Tf₂N], [bmpy][Tf₂N], [perfluoro-hmim][Tf₂N] and [bmim][BF₄] at a temperature range of 283–323 K using a transient thin liquid film method. Their research results show that the measured CO₂ diffusion coefficients in the ILs are dependent on the ionic liquid cation as well as the anion, and the measured CO₂ diffusion coefficients are sensitive to temperature. Heintz *et al.* [74] measured the volumetric liquid-phase mass transfer coefficients of CO₂ and H₂S in the ionic liquid TEGOIL K5 at different temperatures up to 500 K and different pressures up to 3 MPa in a 4 L ZipperClave agitated reactor. Their research results show that the liquid-phase mass transfer coefficients of H₂S in the IL are larger than those of CO₂ in the IL at the temperature range of 300–500 K, which indicates that H₂S can be more easily captured from the dry fuel gas streams and shorter absorbers can be developed for H₂S capture than that for CO₂ capture. Andanson *et al.* [75] investigated the diffusion of the supercritical CO₂ in the IL [bmim][PF₆] at the temperature of 313 K and pressure of 15 MPa with the infrared spectroscopy. Shokouhi *et al.* [82] investigated the diffusion coefficients of CO₂ and H₂S in the IL [hemim][BF₄] at the temperature range of 303.15–353.15 K and pressures up to 1.1 MPa by measuring the absorption kinetics data of CO₂ and H₂S in the IL and using a semi-infinite volume approach. Their research results show that the diffusion coefficients of CO₂ in the IL [hemim][BF₄] are of the same order of magnitude as that of H₂S in the IL. Jalili *et al.* [83] investigated the diffusion coefficients of CO₂ and H₂S in the IL [emim][EtSO₄] at the temperature range of 303.15–353.15 K and pressures up to 1.6 MPa by measuring the absorption kinetics data of CO₂ and H₂S in the IL and using a semi-infinite volume approach. The results show that the diffusion coefficients of H₂S in the IL [emim][EtSO₄] are about two orders of magnitude as that of CO₂ in the IL. Moganty and Baltus [105] measured the diffusion coefficients

of CO₂ under infinite dilution conditions in eight commercially available room-temperature ionic liquids, [emim][Tf₂N], [emim][BETI], [emim][TfO], [emim][TfA], [hmim][Tf₂N], [hmim][BF₄], [Omim][BF₄], and [Bmpy][BF₄], at temperatures of 283.15, 298.15, and 313.15 K using a transient thin liquid film gas uptake technique. Sánchez *et al.* [106] experimentally investigated the reaction kinetics of CO₂ with an amine functionalized ionic liquid at temperatures of 303 and 333 K using the decreasing pressure method in a gas-liquid stirred cell reactor.

The above introduction to the experimental investigations on CO₂ absorption kinetics by ionic liquids indicates that further investigations on CO₂ absorption kinetics by ionic liquids under different operation conditions are needed in order to apply the linear non-equilibrium thermodynamics to analyze the rate-controlling step of the CO₂ absorption kinetics process by ionic liquids and to investigate the effects of different operation parameters on the CO₂ absorption rate.

3.2.2 Vapor-liquid mass transfer area of CO₂ absorption kinetics process by ionic liquids

In order to obtain an accurate CO₂ absorption rate (flux) by ionic liquids in the non-equilibrium thermodynamic model proposed in this paper, both accurate experimental kinetics data and effective mass transfer area are needed. Cross-sectional area was widely used as the vapor-liquid mass transfer area in the investigations of the gas absorption kinetics. However, investigations in the area of surface science show that dissolved gas can exist in the molecular form, as a “solution” in the form of tiny bubbles in nanometer dimensions [107]. Therefore, tiny bubbles of CO₂ may be produced during the CO₂ capture process in ILs. Dong *et al.* [108] and Wang *et al.* [109] investigated the motion of single bubbles in ionic liquids using experimental observations and a numerical simulation, respectively. Wang *et al.* [110] investigated the mass transfer properties of CO₂ capture with ionic liquids using the numerical simulation. They predicted the bubble size distribution and calculated the interfacial area. In this paper, the effective mass transfer area for CO₂ capture with ionic liquids is assumed to be the interfacial area of the tiny CO₂ bubbles produced in the CO₂ capture process, which could be investigated and the CO₂ absorption rate (flux) by ILs could then be further obtained based on recent research results of the nano bubbles and description of the nucleation and growth kinetics of the tiny CO₂ bubbles in the CO₂ capture process by ILs, combined with experimental kinetics data of the CO₂ capture by ILs, and the material conservation principles.

3.3 Interfacial transfer rate of CO₂(IL) in CO₂ capture process by ILs

In recent available investigations on CO₂ dissolution kinetics, the concentration of component *i* at the vapor-liquid

interface at any time is considered to be the instantaneous equilibrium concentration. In the absorption kinetics investigations of CO₂ and H₂S in the ionic liquid TEGOIL K5 performed by Heintz *et al.* [74], an instantaneous equilibrium at the interface was considered. In the CO₂ dissolution kinetics investigations in brines by Ji *et al.* [111], the concentration of CO₂(aq) at the vapor-liquid interface was considered as the instantaneous equilibrium concentration. However, the investigations of Ward *et al.* showed that the usual assumption of the instantaneous equilibrium at the liquid-gas interface may lead to the illogical consequence [112], and they developed the statistical rate theory (SRT) to describe the molecular transport rate at the vapor-liquid and solid-liquid interfaces based on a first-order perturbation analysis of the Schrödinger equation and the Boltzmann definition of entropy [113–115]. In this paper, SRT is used to describe the molecular transport rate at the vapor-liquid interface, and the rate expression is composed of the following three parts [114] as shown in eq. (4): (a) the chemical potential of the molecules in the vapor phase; (b) the chemical potential of the molecules in the liquid solution at the vapor-liquid interface; (c) the equilibrium exchange rate between the vapor and liquid phases k_e .

$$J = k_e \left[\exp\left(\frac{\mu^g - \mu^l}{\kappa T}\right) - \exp\left(\frac{\mu^l - \mu^g}{\kappa T}\right) \right] \quad (4)$$

In eq. (4), k_e is the equilibrium exchange rate between the vapor and liquid phases; μ^g is the chemical potential of the molecules in the vapor phase; μ^l is the chemical potential of the molecules in the liquid solution at the vapor-liquid interface; κ is the Boltzmann constant and T is the temperature.

Eq. (4) shows that the description of the interfacial transfer rate of CO₂(IL) in the CO₂ capture process by ILs also needs the reliable thermodynamic models to calculate the chemical potential of the systems.

4 Conclusions and perspectives

Ionic liquids show broad prospects for CO₂ capture, and their application requires fundamental thermodynamic research. Accurate fundamental data concerning the thermodynamic properties and phase equilibrium of the systems are important basis. The process rate is important to determine the feasibility of the process.

Based on the non-equilibrium thermodynamic model of CO₂ absorption kinetics by ionic liquids proposed in this paper, the following further investigations are needed:

(1) To develop reliable thermodynamic models: the molecular thermodynamic models such as SAFT EoS and SWCF EoS have been successfully used to describe the phase behaviors of the CO₂-ionic liquid systems and show excellent potential for applications in engineering. However, more investigations of the thermodynamic properties for

more CO₂-ionic liquid systems need to be further performed.

(2) To describe the interfacial transport rate: SRT is used to describe the molecular transport rate at the vapor-liquid interface.

(3) To investigate the CO₂ absorption kinetics by ionic liquids: recently there have been less experimental investigations on CO₂ absorption kinetics by ionic liquids, and a large number of experimental kinetics studies focus on the CO₂ diffusion coefficient in ionic liquids, while the experimental kinetics data that could be used to analyze the rate-controlling step of CO₂ absorption by ionic liquids using the linear non-equilibrium thermodynamic modeling proposed in this paper have rarely been reported. Further investigations on CO₂ absorption kinetics by ionic liquids under different operation conditions are needed.

(4) Vapor-liquid mass transfer area of CO₂ absorption kinetics process by ionic liquids: in this paper, the effective mass transfer area for CO₂ capture with ionic liquids is assumed to be the interfacial area of the tiny CO₂ bubbles produced in the CO₂ capture process, which could be investigated and the CO₂ absorption rate (flux) by ILs could then be further obtained based on recent research results of the nano bubbles and description of the nucleation and growth kinetics of the tiny CO₂ bubbles in the CO₂ capture process by ILs, combined with experimental kinetics data of the CO₂ capture by ILs and the material conservation principles.

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