Perspective

The Solubility of Gases in Ionic Liquids

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In this Perspective, we provide a detailed discussion of the techniques and methods used for determining the solubility of gases in ionic liquids (ILs). This includes various experimental measurement techniques, equation of state (EOS) modeling, and predictive molecular-based modeling. Many of the key papers from the past 15 years are discussed and put into the context of the latest advances in the field. Limitations of these methods plus future developments and new research opportunities are discussed. © 2017 American Institute of Chemical Engineers *AIChE J*, 63: 4722–4737, 2017
Keywords: ionic liquids, gas solubility, absorption, phase equilibria, isotherm, modeling

History of ILs

The first observations of materials we now recognize as ILs are believed to date back as far as the mid-nineteenth century, when Friedel and Crafts described the formation of a "red oil," which often appeared in their alkylation and acylation reactions.[1,2] The red oil, which was identified almost a century later by chemists in Japan, consisted of an alkylated aromatic ring cation and a chloroaluminate anion, which by definition was an IL.[1,3] Paul Walden in 1914 is credited with publishing the first scientific paper that described the synthesis of the room-temperature IL ethylammonium nitrate, which has a melting point of 12.5°C.[4] However, it was not until 1992 when John Wilkes and Michael Zaworotko at the U.S. Air Force Academy reported the synthesis of the first "air and water stable" imidazolium ILs, such as 1-ethyl-3-methylimidazolium hexafluorophosphate and 1-ethyl-3-methylimidazolium tetrafluoroborate, that the field began to expand.[5] Wilkes later wrote one of the first review papers on ILs entitled "A short history of ionic liquids – from molten salts to neoteric solvents."[6]

In April 2000, the first NATO advanced research workshop (ARW) on ILs was held in Heraklion, Crete. The conference was the first international meeting devoted to ILs and attracted most of the active researchers at that time. Following that meeting, activity in the field began to flourish and the first books and international conferences devoted to ILs began to appear.

The first book dedicated to ILs was edited by Kenneth Seddon and Robin Rogers in 2002 entitled "Ionic Liquids, Industrial Applications to Green Chemistry."[7] This book contained the key papers from the American Chemical Society National Meeting symposium, "Green (or Greener) Industrial Applications of Ionic Liquids" held in San Diego, California, April 1–5, 2001. The symposium was the first "open" international meeting on the fundamentals and applications of ILs (the NATO ARW meeting held in Crete was by invitation). Another seminal text that appeared in 2002 edited by Peter Wasserscheid and Tom Welton was entitled "Ionic Liquids in Synthesis."[8] The book was designed to take the reader from little or no knowledge of ILs to an understanding reflecting the best knowledge at that time. These authors are now eminent scholars in the field of ILs.

A number of other excellent books have been written about ILs, some which now specialize in particular fields of use such as organic synthesis, electrochemistry, bio-processing, pharmaceuticals, catalysis, separations, and industrial applications.[1,9–36] The field has rapidly expanded, and a recent Scifinder and Web of Science search using the key word "ionic liquid" estimates that over 20,000 publications and 4,000 patents have been published since 2012 (i.e., over 100 references per week for the past 5 years).

The solubility of gases has played an important role in the history of ILs, which traditionally have been considered as new solvents for both separations and chemical reactions.[7–36] In gas separations, the design of the absorption (desorption) column requires solubility data for the gases in the ILs. In gas–liquid reactions such as alkylation, hydrogenation, and hydroformylation, the mass transfer of the gas in the IL phase is needed to design the chemical reactor. Other applications which require knowledge of gas solubility in ILs include absorption cooling, polymerization, membranes, lubrication, extraction, and gas-expanded liquids to name a few.

Gas Solubility in ILs

ILs are defined as molten salts with a melting temperature below about 373 K.[8,15,16] ILs have received significant attention

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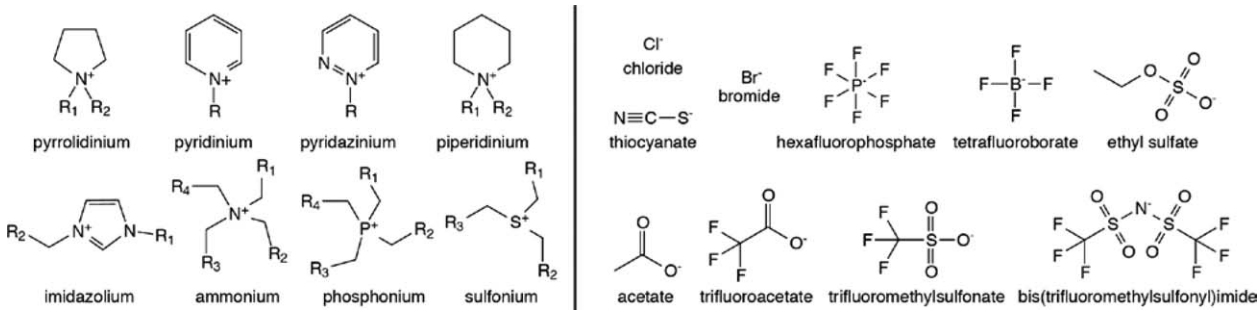

Figure 1. Chemical structure for common cations and anions.

due to their low vapor pressure, high chemical and thermal stability, and the large variety of cations and anions that can be synthesized.[8,15,16] Figure 1 provides the structures for some of the most common cations and anions.

A variety of thermophysical property data have been published for ILs. The NIST Ionic Liquids Database (ILThermo v2.0)[37,38] is a free web research tool that allows users worldwide to access an up-to-date data collection from publications on experimental studies of thermodynamic and transport properties of ILs. The database contains gas solubility data as well as information on chemical identification, sample purity, phase transitions, transport, volumetric and thermal properties, surface tension, refractive index, speed of sound, vapor pressure, and activity coefficients with details of experimental methods and numerical data uncertainty.

A recent literature search found over 200 references published in the past 5 years (2012–2017) on the "solubility of gases in ionic liquids," and a recent review by Lei et al. in 2014 provides the solubility for several gases (H_2, O_2, N_2, CO, CO_2, Ar, Xe, Kr, SO_2, H_2S, N_2O, NO_2, NH_3, H_2O, hydrocarbons, and hydrofluorocarbons) in a variety of ILs with over 350 references.[39] The results are often reported as the Henry's Law constant; however, we believe that the description of gas solubility in ILs should include the global phase behavior (i.e., vapor–liquid equilibria [VLE], vapor–liquid–liquid equilibria [VLLE], and liquid–liquid equilibria [LLE]).[40,41]

The main focus of this Perspective is to emphasize the importance of characterizing the complete phase behavior (i.e., gas mole fraction from $0 \leq x \leq 1$) over a wide temperature and pressure range and utilizing simulation tools to understand the molecular interactions. Several gas + IL systems exhibit both miscible (VLE) and immiscible regions (VLLE and LLE) that can be classified according to the type of high-pressure phase behavior defined by van Konynenburg and Scott.[42,43] To understand such a wide range of phase behavior, EOS methods are required and one will be briefly described.

Initially, we had some doubt about whether a nonelectrolyte EOS could work for IL mixtures; however, the EOS method works well for *PVTx* phase calculations. This should not be surprising, because the thermodynamic equilibrium for VLE does not depend on knowing the structure of the liquid. Here, molecular simulations can provide a detailed understanding of the gas + IL interactions.

VLE Measurements

To accurately measure the solubility of a gas in an IL requires: (i) purification and characterization of the solute gas and IL; (ii) thorough drying and degassing of the IL; (iii) equilibration of the gas and IL phases under the conditions of known constant temperature and pressure; (iv) measurements that determine the composition of the gas in the IL phase; (v) proper error analysis to estimate the uncertainty; and (vi) use of a thermodynamic model to validate results.[41] Any paper reporting data on the solubility of a gas in a IL should include an adequate description of these steps and comparison measurements on a standard system to allow the user to judge the reliability of the data.[44] For this purpose, the International Union of Pure and Applied Chemistry (IUPAC) sponsored a project to make physical property measurements available for comparing the gas solubility of CO_2 in a reference IL, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (commonly abbreviated [hmim][Tf_2N], [C_6mim][NTf_2], or [C_6C_1im][Tf_2N]).[45,46] The report provides both recommended gas absorption methods and reference values for VLE and LLE of CO_2 in [C_6C_1im] [Tf_2N].[46]

A variety of experimental methods have been used to measure the solubility of gases in ILs including physical methods (gravimetric and synthetic) and analytical methods (chromatographic and spectroscopic).

Gravimetric method

A common technique used to measure the solubility of gases in ILs is the gravimetric method. Although this method was originally developed to measure gas adsorption on solids such as zeolites and carbons, it can be applied to ILs because their extremely low vapor pressure prevents evaporation of the sample. This technique was used by Maginn and Brennecke who published some of the first papers on the solubility of gases in ILs.[47–49] The advantages of a microbalance include the minimal sample size required (<100 mg IL), the ability to measure both gas solubility and diffusivity simultaneously,[50] and the flexibility to acquire absorption and desorption isotherms. Figure 2 provides a schematic of a Hiden gravimetric microbalance (XEMIS).[51]

Synthetic methods

Several variations of the synthetic (or stoichiometric) method exist, which involve adding a precise amount of gas and IL into a high-pressure view cell with a known volume.

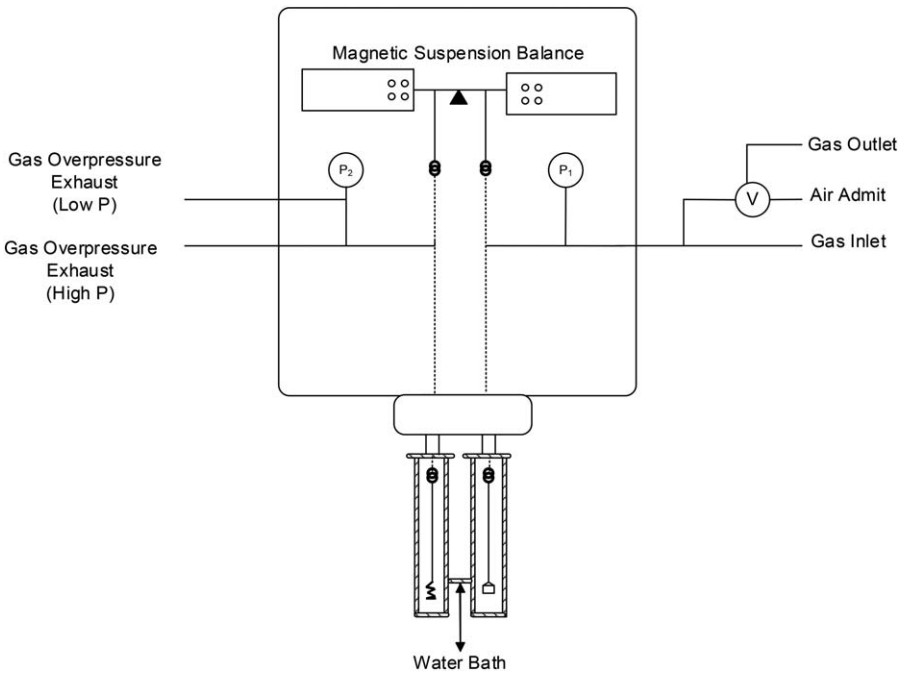

Figure 2. Schematic diagram of Hiden Isochema XEMIS gravimetric microbalance.[51]

One method used by several researchers involves increasing the pressure (at constant temperature) until all the gas dissolves in the IL and the last bubble disappears (bubble point method).[52–60] A variation of this method involves continuing continuously increasing the pressure using a variable-volume view cell and then slowly decreasing the pressure until the first bubble appears.[61] Maurer and coworkers have used a similar method, but observe the phase change by adding and withdrawing known amounts of the IL to pressurize (depressurize) the mixture.[62–65] The method developed by Ren and Scurto measures the vapor and liquid phase volumes and calculates the solubility, molar volume, volume expansion, and density of the liquid solution.[66–68]

A pressure drop method is also used with a calibrated gas volume (V_1) at a given T and P. A known amount of IL is added to a second calibrated volume (V_2) which is connected by a valve to V_1. When the valve is opened the gas fills both volumes and dissolves in the IL. Measurement of the pressure drop at equilibrium allows the number of moles of gas to be calculated in the vapor and liquid phase (by difference). This technique has been used by Costa Gomes and coworkers in glassware at low pressures and is ideal for measuring dilute solutions to obtain Henry's Law constants.[69–73]

Chromatographic methods

Gas chromatography (GC) has been used to measure infinite dilution activity coefficients and the equivalent Henry's Law constants. A chromatography column is coated with an IL and the solute (gas or liquid) is introduced with a carrier gas. The retention time of the solute is measured at steady state, and the strength of the interaction of the solute in the IL determines the infinite dilution activity coefficient. This technique has been used by Heintz et al. to measure the infinite dilution activity coefficients of liquids in ILs.[74–76]

Spectroscopic methods

Infrared and ^{1}H-NMR spectroscopy has been used to measure the solubility of gases in ILs. Welton and coworkers used ATR-IR and ^{1}H-NMR to measure the solubility of carbon dioxide and hydrogen in ILs, respectively.[77] UV–vis absorption, Raman, ^{1}H-NMR and ^{13}C-NMR spectroscopy have been used to characterize the interactions between gases and ILs.[78]

LLE Measurements

LLE measurements have been successfully conducted using a simple mass–volume technique.[79,80] When a binary system exhibits a liquid–liquid separation (or VLLE), it is an *univariant* state according to the Gibbs phase rule. This means that at a given intensive variable, for example, temperature, there is no freedom for other intensive variables. All other variables such as compositions, pressure, and densities of the system are uniquely determined regardless of any different extensive variables (volume of each phase and total mass of the system). The overall feed composition merely changes the physical volume in each phase, but the composition and density in each phase remains constant as long as the three phases exist at the fixed T.

This unique VLLE state of a binary system can be determined experimentally using a simple apparatus by mass and volume measurements *alone* without using any analytical method for the composition analysis. A set of mass and volume measurements of two sample containers at a constant temperature is sufficient to determine the required thermodynamic properties.[79,80]

Mixing time to reach equilibrium can take several hours to days and is one of the most critical properties for properly measuring VLLE whether using this method or the more common cloud-point method.[81–86] The time required to effectively

mix the gas + IL systems and reach equilibrium depends on the choice of IL, the gas and the solution viscosity.

Modeling Gas Solubility

Measuring and reporting the solubility of a gas in an IL does not ensure that the results are thermodynamically consistent. A thermodynamic model should be applied to check the data quality and can be useful in making predictions. The thermodynamic phase behaviors of gases with ILs can be well modeled with activity models and EOS methods.[87,88]

Several activity models are available in the literature[89–91] and the experimental (*PTx*) results have been analyzed using the nonrandom two liquid model.[92–94] However, activity models (or any solution models) are inaccurate (or undefined) at high temperatures, particularly near and above the T_c of the gaseous species. Therefore, extrapolations for phase behaviors over wide T and P ranges must be treated with caution. Also, the prediction of LLE based only on VLE data, or vice versa, is not numerically accurate with any conventional activity model.[90] More reliable predictions of the global phase behavior can be made using an EOS.

EOS modeling

A variety of EOS models have been reported[39] to describe phase behavior of gases in ILs such as the generic Redlich–Kwong (RK) type of cubic EOS[95,96]

$$P=\frac{RT}{V-b}-\frac{a(T)}{V(V+b)} \tag{1}$$

$$a(T)=0.427480\frac{R^2T_c^2}{P_c}\alpha(T) \tag{2}$$

$$b=0.08664\frac{RT_c}{P_c},\quad (R:\ \text{universal gas constant}) \tag{3}$$

The temperature-dependent part of the (a) parameter in the EOS for pure compounds is modeled by the following empirical equations[96]

$$\alpha(T)=\sum_{k=0}^{\leq 3}\beta_k(1/T_r-T_r)^k,\ \text{for}\ T_r\equiv T/T_c\leq 1 \tag{4a}$$

$$\alpha(T)=\beta_0+\beta_1[\exp\{2(1-T_r)\}-1],\ \text{for}\ T_r\geq 1 \tag{4b}$$

The coefficients, β_k, are determined so as to reproduce the vapor pressure of each pure compound. It should be noted that Eq. 4b is implemented for $T_r\geq 1$ in order for $\alpha(T)$ to be physically meaningful for gases even at very high temperatures. Equation 4b is always $\alpha(T)>0$ and a decreasing function with T. When $T_r=1$, Eqs. 4a and 4b are set to be analytically continuous.

Typically for ILs, no vapor pressure data are available because they are practically nonvolatile. Also, estimated data for the critical parameters (T_c and P_c) exist[97–102]; however, only rough estimates are required for the present EOS modeling. The T_c are hypothetical values because they are above the decomposition T for ILs. On the other hand, the temperature-dependent part of the a parameter of ILs (Eq. 2) is significant when trying to correlate the solubility (pressure-temperature-composition: *PTx*) data, despite the vapor pressure of ILs being essentially zero at the temperature of interest. Therefore, the coefficient β_1 for ILs in Eq. 4 is usually treated as an adjustable fitting parameter using $\beta_0=1$ and $\beta_2=\beta_3=0$ in the solubility data analysis, together with the binary interaction parameters discussed below. However, once β_1 is determined for a particular IL using a certain binary system, it is used as a fixed constant for any other binary systems containing that IL.

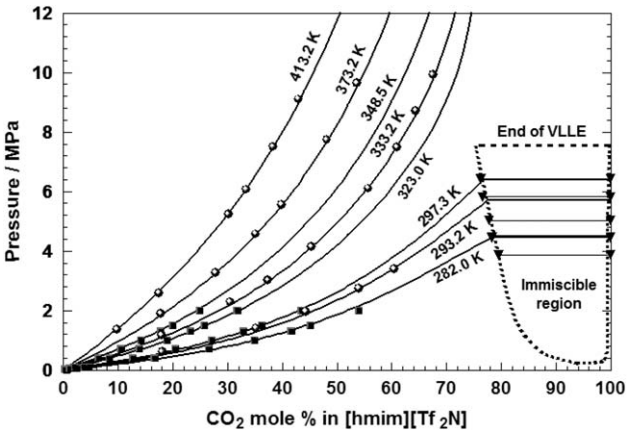

Figure 3. Isothermal P_x phase diagram for CO_2 + [hmim][Tf_2N] (i.e., [C_6C_1im][Tf_2N]).

Solid lines: calculated using the EOS model.[87] Symbols: ●, VLE data[64]; ■, VLE data[87]; ▼, VLLE data[87]; figure was used with permission.[87]

The a and b parameters for a general N-component mixture are modeled in terms of binary interaction parameters[95]

$$a=\sum_{i,j=1}^{N}\sqrt{a_ia_j}\,f_{ij}(T)(1-k_{ij})x_ix_j,\qquad a_i=0.427480\frac{R^2T_{ci}^2}{P_{ci}}\alpha_i(T) \tag{5}$$

$$f_{ij}(T)=1+\tau_{ij}/T,\qquad \text{where}\quad \tau_{ij}=\tau_{ji},\quad \text{and}\quad \tau_{ii}=0 \tag{6}$$

$$k_{ij}=\frac{l_{ij}l_{ji}(x_i+x_j)}{l_{ji}x_i+l_{ij}x_j},\qquad \text{where}\quad k_{ii}=0 \tag{7}$$

$$b=\frac{1}{2}\sum_{i,j=1}^{N}(b_i+b_j)(1-k_{ij})(1-m_{ij})x_ix_j,\qquad b_i=0.08664\frac{RT_{ci}}{P_{ci}} \tag{8}$$

where $m_{ij}=m_{ji}$, and $m_{ii}=0$; T_{ci}, critical temperature of ith species; P_{ci}, critical pressure of ith species; and x_i, mole fraction of ith species.

The present EOS model has been successfully applied to a variety of gas + IL systems.[40,41,87,88] Figure 3 provides a comparison of experimental *PTx* data (CO_2 + [C_6C_1im][Tf_2N]) from the IUPAC project fitted with the RK EOS model.[87] The standard deviation for the P versus x_1 fit is excellent (± 0.03 MPa). The EOS model also predicts a partial immiscibility in CO_2-rich solution which has been confirmed using the mass–volume technique to measure LLE behavior as shown in Figure 3. The CO_2 + [C_6C_1im][Tf_2N] system likely exhibits the Type-III mixture behavior according to the classification of van Konynenburg and Scott.[42,43] In this case, the LLE will intersect with the solid–liquid equilibria such that no lower critical solution temperature (LCST) can exist. In other systems containing hydrofluorocarbons in ILs (CHF_3 + 1-butyl-3-methylimidazolium hexafluorophosphate {[C_4C_1im][PF_6]}, CH_2FCF_3 +

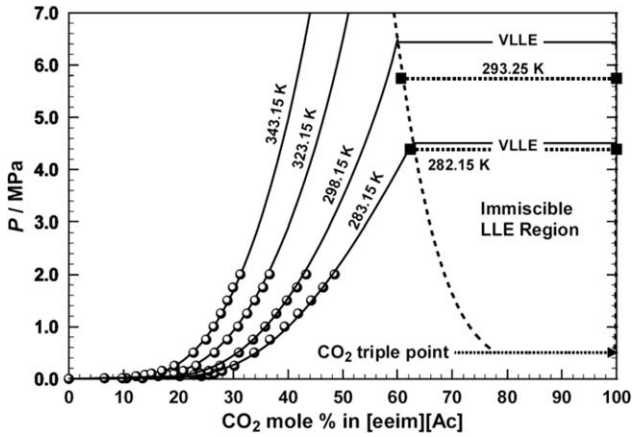

Figure 4. Isothermal P_x phase diagram for CO_2 + [eeim][Ac] (i.e., [C_2C_2im][C_1CO_2]).

Solid lines: calculated using the EOS model.[105] Symbols: ●, VLE data[105]; ■, VLLE data[105]; figure was used with permission.[105]

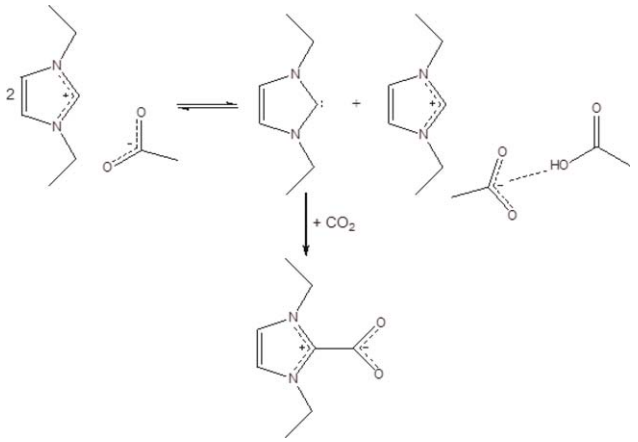

Figure 5. Proposed reaction mechanism for CO_2 + [eeim][Ac] (i.e., [C_2C_2im][C_1CO_2]).[105–108]

Figure was used with permission.[105–108]

$[C_4C_1im][PF_6]$, $CH_3CHF_2 + [C_4C_1im][PF_6]$, $CH_3CH_2F + [C_4C_1im][PF_6]$), the existence of a LCST supports the Type-V mixture behavior.[80,88] Pure component EOS constants, optimal binary interaction parameters (l_{ij}, l_{ji}, m_{ij}, and τ_{ij}), fugacity coefficient, and other derived thermodynamic properties for the CO_2 + [C_6mim][Tf_2N] system are provided in Ref. 87.

Carbon dioxide possesses relatively high solubility in ILs; however, most cases are for physical-type absorption.[41,49,51–55,57–61,63,66,68–72,77,87] Other cases exist such as with CO_2 and ILs containing an acetate anion (e.g., 1-butyl-3-methylimidazolium acetate [C_4C_1im][C_1CO_2], 1-ethyl-3-methylimidazolium acetate [C_2C_1im][C_1CO_2] and 1-ethyl-3-ethylimidazolium acetate [C_2C_2im][C_1CO_2]) where highly negative deviations from Raoult's law indicate chemical absorption instead of ordinary physical absorption.[103–105] As shown in Figure 4, the negative deviation is so large that the pressure of CO_2 gas becomes practically zero at CO_2 mole fraction range of less than about 0.3 (30 mole %).[105] The proposed mechanism shown in Figure 5 has been confirmed experimentally by several research groups.[103–108]

To understand the physical meaning of such highly non-ideal phase behavior consider the following two types of chemical absorption behavior for species A and B in a liquid solution[109–114]

$$A + B = AB, \text{ with an equilibrium constant } K_1 \quad (9)$$

$$A + 2B = AB_2, \text{ with an equilibrium constant } K_2 \quad (10)$$

Therefore, in solution, there can exist four species: A, B, AB, and AB_2. If we assume that these species form an *ideal solution*, then the following thermodynamic excess functions can be derived[109–114]

$$\frac{G^E}{RT} = (1-x_B)\ \ln\frac{1-z_B}{(1-x_B)(1+K_1z_B+K_2z_B^2)} + x_B\ \ln\frac{z_B}{x_B} \quad (11)$$

$$\frac{H^E}{RT} = \frac{(1-x_B)z_B(K_1\Delta H_1 + K_2\Delta H_2 z_B)}{RT(1+K_1z_B+K_2z_B^2)} \quad (12)$$

where x_B = the stoichiometric (or feed) mole fraction of species B, z_B = the true (or actually existing) mole fraction of B in the solution, and ΔH_1 and ΔH_2 are the heats of complex formation for the association reactions of Eqs. 9 and 10, respectively. x_B is related to z_B by[109,110]

$$x_B = \frac{(1+K_1)z_B + K_2z_B^2(1-z_B)}{1+K_1z_B(2-z_B)+K_2z_B^2(3-2z_B)} \quad (13)$$

Using the present EOS, the excess functions, G^E and H^E, can be calculated at given T, P, and compositions (see Eqs. S29, S31, and S32 in supporting information of Ref. 105). Species A is designated as CO_2 and B as the IL. The temperature is taken as 298.15 K, and $P = 6.5$ MPa, which is close to the vapor pressure of CO_2 at 298.15 K. Then, G^E and H^E from the EOS correlation can be calculated as a function of x_A ($=1-x_B$) as shown in Figure 6.[105] Also, G^E and H^E from the association model can be evaluated similarly as a function of x_B ($=1-x_A$) with four unknown parameters K_1, K_2, ΔH_1, and ΔH_2; see Eqs. 11–13. These unknown parameters are determined by minimizing the differences of both G^E and H^E functions between the EOS and the association models using a

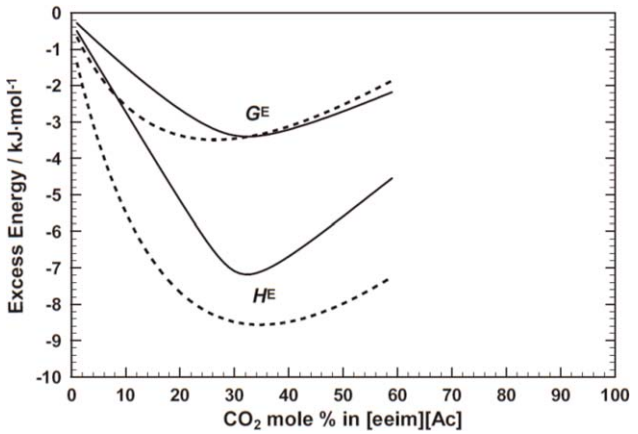

Figure 6. Analysis of the ideal association model using an example of CO_2 + [eeim][Ac] (i.e., [C_2C_2im][C_1CO_2]).

Solid lines: the EOS model calculation. Dotted lines: results from the association model by the least-squares analysis of G^E and H^E; figure was used with permission.[105]

nonlinear least-squares method.[105] The mole fraction range used in the analysis is $0 < x_A < 0.6$, since solutions with higher CO_2 mole fractions (about > 0.7) become immiscible liquids, as mentioned earlier. Trial-and-error analyses show that only one type of the complex (AB_2) is dominating in the present liquid solution ($CO_2 + [C_2C_2im][C_1CO_2]$). This fact is consistent with the observation of the minimum G^E location of about $x_A = 0.33$ shown in Figure 6 and consistent with the mechanism shown in Figure 5 that two moles of $[C_2C_2im][C_1CO_2]$ are required per mole of CO_2 (2:1 $[C_2C_2im][C_1CO_2]$:CO_2).[105–108] This highly asymmetric phase behavior with respect to concentration is extremely rare,[115] and one of the only other known examples is a binary system of HCl and water.[115,116] Similar behavior has been calculated for the $CO_2 + [C_2C_1im][C_1CO_2]$ and $CO_2 + [C_4C_1im][C_1CO_2]$ binary systems.[103,104] It is important to mention that in all three cases ($[C_2C_1im][C_1CO_2]$, $[C_2C_2im][C_1CO_2]$, $[C_4C_1im][C_1CO_2]$) the binary systems show the liquid–liquid separation (immiscibility) at high CO_2 concentrations (higher than about 0.7 mole fraction CO_2).[103–105]

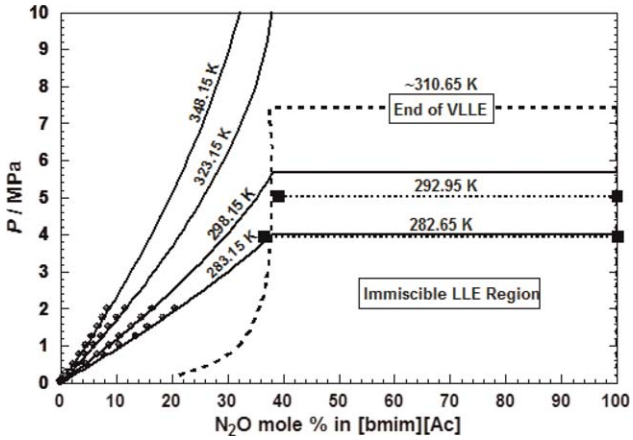

Figure 7. Isothermal P_x phase diagram for $N_2O + [bmim][Ac]$ (i.e., $[C_4C_1im][C_1CO_2]$).

Solid lines: calculated using the EOS model.[123] Symbols: ●, VLE data[123]; ■, VLLE data[123]; figure was used with permission.[123].

Gas Separation

An EOS model for a ternary system has been developed to evaluate the effectiveness of ILs for gas separation.[117–123] Pure component and binary interaction parameters can be determined using the same procedures as discussed for the RK EOS model; however, the phase behavior prediction of the *ternary system* may not always be guaranteed based on the binary interaction parameters alone. In particular for systems containing supercritical fluids and/or nonvolatile compounds such as ILs, the validity of an EOS model for ternary mixtures must be checked experimentally. Ternary VLE experiments are not widely available in the literature and are a very sensitive check of the EOS model.

There have been an extremely large number of experimental and computational studies devoted to the solubility of CO_2 in ILs.[124] Much of this has been driven by the concept of using ILs for CO_2 capture. Most work in this area has focused on determining pure component isotherms for CO_2 and other gases such as N_2, O_2, and H_2O. To understand the ability of an IL to separate CO_2 from other gases such as N_2, however, one needs to perform mixed gas experiments or simulations. It is much more difficult to perform mixed gas experimental solubility measurements than pure component studies, and so most studies have focused on pure gas solubilities and assumed ideal mixing to estimate the separation capacity of an IL for a mixed-gas system.[125,126] Such an approximation is probably justified when gas solubility is low, such that the solution behaves ideally. As gas solubility increases, however, it is unlikely that pure gas solubilities can predict mixed gas solubilities with a high degree of accuracy. What is needed are more experimental and computational studies devoted to mixed gas solubilities in ILs.

One system where this has been done is gas mixtures of N_2O and CO_2 in the IL (1-butyl-3-methylimidazolium acetate $[C_4C_1im][C_1CO_2]$), but there are other systems.[117–123] Ternary VLE measurements were performed using a GC method to analyze the vapor composition which confirmed the validity of the ternary EOS model.[117–123] Figure 7 is a *PTx* phase diagram for $N_2O + [C_4C_1im][C_1CO_2]$ which shows physical absorption with a large immiscibility (LLE) region that suggests this binary system likely exhibits Type III phase behavior. The $CO_2 + [C_4mim][C_1CO_2]$ system was previously measured[103] and the VLE data for $N_2O + CO_2$ was obtained from the literature.[127]

Now that the present EOS model has been verified, the solubility behavior of the present ternary system can be predicted with confidence. To assess the feasibility of the gas separation by extractive distillation or selective absorption processes, the selectivity $\alpha_{A/B}$ for gases A and B in the gas phase, or the absorption selectivity $S_{B/A}$ for A and B in the liquid phase is commonly defined

$$\alpha_{A/B} = S_{B/A} = \left(\frac{y_A}{x_A}\right) / \left(\frac{y_B}{x_B}\right) \tag{14}$$

where x_A (or x_B) and y_A (or y_B) are the mole fractions of A (or B) in the liquid phase and vapor phase, respectively.[128] For this example, N_2O is A and CO_2 is B. The N_2O/CO_2 selectivity ($\alpha_{A/B}$) in the gas phase has been examined using the present EOS model at various T, P, and feed compositions.[123] In Figure 8a, the N_2O/CO_2 selectivity ($\alpha_{A/B}$) is plotted as a function of the IL $[C_4mim][C_1CO_2]$ concentration for ternary mixtures with three N_2O/CO_2 mole ratios (3/1, 1/1, and 1/3) at $T = 298.15$ K and $P = 0.1$ MPa. The selectivity ($\alpha_{A/B}$) increases dramatically with the addition of the IL $[C_4C_1im][C_1CO_2]$ (greater than ca. 60 mole%).

To understand the change in selectivity due to the IL addition, Figure 8b provides clear insights, showing the selectivity *without* $[C_4C_1im][C_1CO_2]$ at 298.15 K as a function of pressure for the same N_2O/CO_2 feed ratios (3/1, 1/1, and 1/3). The selectivity enhancement due to the IL addition can be easily observed from the comparison between Figures 8a, b. The three feed ratios (3/1, 1/1, and 1/3) with the IL have a selectivity of about 1×10^3 to 1×10^7, while the corresponding case *without* the IL shows a selectivity of about 0.96. Without the use of the IL the N_2O/CO_2 separation is not practical.

Previous work using $[C_4C_1im][BF_4]$ as the entrainer achieved only a selectivity of 1.5.[122] The 3 to 7 orders of magnitude increase in selectivity using $[C_4C_1im][C_1CO_2]$ shows

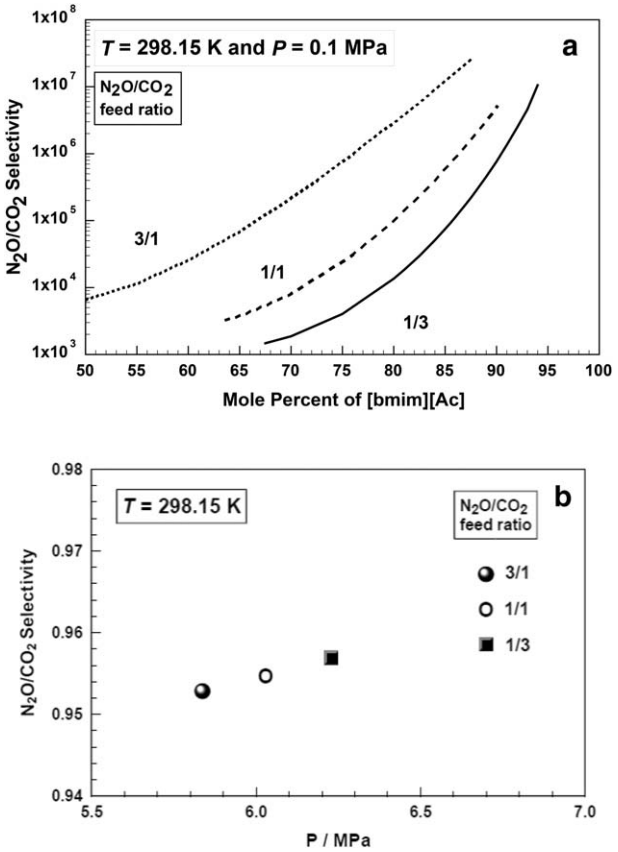

Figure 8. (a) Plots of calculated N_2O (A)/CO_2, (B) selectivity defined by Eq. (14) *versus* overall [bmim][Ac] (i.e., [C_4C_1im][C_1CO_2]), (C) mole fraction with three different N_2O/CO_2 feed ratios at $T = 298.15$ K and $P = 0.1$ MPa.

(b) Selectivity plots without IL [bmim][Ac] (i.e., [C_4C_1im][C_1CO_2]) as a function of total pressure. Three cases with different N_2O/CO_2 feed ratios are shown at $T = 298.15$ K. Lines: dotted line, 3/1 N_2O/CO_2 feed mole ratio; broken line, 1/1 N_2O/CO_2 feed mole ratio; solid line, 1/3 N_2O/CO_2 feed mole ratio. Figures were used with permission.[123]

the significance that the choice of IL can make in this separation. As shown in Figures 4 and 5, the acetate containing ILs chemically interact with CO_2.[103–106] This strong chemical attraction significantly increases the selectivity over N_2O which demonstrates physical absorption behavior as shown in Figure 7. To our knowledge this is the *largest selectivity difference* ($\alpha = 1 \times 10^3$ to 1×10^7) ever demonstrated for a gas separation using an IL and clearly shows the utility of these novel materials as entrainers.

Although N_2O is not the major contributor to global warming (~6%), it is one of six greenhouse gases (CO_2, CH_4, N_2O, HFC, PFC, and SF_6) identified for reduction by the United Nations Framework on Climate Change (UNFCC).[129] As a result, a number of industries have voluntarily initiated efforts to reduce N_2O emissions, particularly from power plants and adipic acid production; therefore, ILs may play an important role in the separation of N_2O from CO_2.[123]

Predictive Computational Modeling of Gas Solubility in ILs

Given the huge number of possible ILs and the time and expense associated with conducting detailed experimental solubility measurements, a great deal of effort has been directed at developing theoretical or computational methods that can predict phase equilibria for gas-IL systems. Almost all of these methods can be classified into one of three categories: (1) correlative methods that relate molecular-level descriptors to limited experimental data; (2) hybrid quantum chemical/statistical thermodynamics approaches; and (3) atomistic force field-based simulation methods. The latter two categories are the most "predictive" since, in principle, they do not require experimental data as input. They are also the most computationally intensive. The correlative methods are extremely fast, but do require significant amounts of experimental data and often do not extend well beyond the classes of systems for which the models were developed. A short review of each approach is provided next along with possible limitations and future developments of the methods.

Correlative methods

Correlative methods seek to find statistical relationships between a property of interest (i.e., gas or vapor solubility) and a set of molecular descriptors that describe such things as the structural, topological, chemical and electronic characteristics of the molecules under consideration. The idea is to develop the correlations on a training set of experimental data and then apply it to make predictions for similar compounds outside the training set. These methods are generally referred to as quantitative structure property relationship (QSPR) models[130] and have been shown to do an excellent job correlating (and in some cases, predicting) gas solubility in ILs.

Eike at al.[131] were the first to use QSPR to estimate the solubility of organic solutes in ILs. They proposed a set of four-parameter QSPR models for the infinite-dilution activity coefficients γ^∞ of 38 organic solutes in three different ILs. These systems were chosen because high-quality experimental data were available from the Heintz group.[74–76]

Other researchers have carried out similar studies. Tämm and Burk[132] developed an improved QSPR model for the same system as that studied by Eike at al. using only three parameters. Katritzky et al. developed two- to four-parameter models for the partition coefficients of organic solutes in eight different ILs.[133] Recently, QSPR models have been used to examine CO_2[134,135] and H_2S[136] solubility in ILs.

In a related approach, QSPR correlations have been developed for gas-to-solvent and water-to-solvent partition coefficients for a range of solute-IL systems using the Abraham model,[137] in which the descriptors are the excess molar refraction and dipolarity/polarity of the solute, the solute hydrogen-bond acidity and hydrogen bond basicity, and the McGowan volume of the solute.[138] This approach correlates experimental data very well, but like other QSPR methods, it suffers from the fact that a separate QSPR expression is required for each IL. This prevents one from "designing" new ILs with a desired γ^∞ for a given solute. To overcome this, various group contribution methods have been proposed in which cation- and anion-specific coefficients are determined and used in a linear solvation model.[139] These methods all used relatively simple

multilinear models to perform the correlations, and accuracies within 20%–30% of experimental data were typically obtained.

Advanced neural networks and machine learning techniques have also been applied to develop more robust models for solubility in ILs.[140–143] Paduszyński has reviewed much of this and previous QSPR work and then used three different machine learning algorithms to develop new QSPR models for infinite dilution activity coefficients in ILs.[144] As neural network and machine learning techniques continue to advance, it is likely that they will play an increasingly important role in developing highly accurate solubility models. Crucial to this effort, however, is the availability of extensive, validated data. Up until now, only experimental solubility data have been used in developing these models; it will be interesting if some of the data generated by other methods is used to estimate solubilities (described below) in the future when developing these models.

Hybrid quantum/statistical thermodynamics methods

Solvation is a collective phenomenon involving a complex interplay of interactions between the solute and the solvent molecules. Physics-based predictive models must account for these interactions. While quantum chemical methods can obtain very accurate energies of interaction between individual molecules, they are difficult to apply directly to compute solubilities for two reasons. First, solvation effects involve specific interactions between many molecules, making the use of highly accurate quantum methods expensive. Second, to properly consider entropic effects, a large number of configurations of the solute and solvent molecules should be sampled. Again, such calculations are prohibitively expensive with brute force quantum chemical methods. Researchers have attempted to use small cluster models to understand solvation trends[145] but the results are typically qualitative and do not provide macroscopic solubility predictions. As a result, approximate solvation models are often used in combination with quantum chemical methods to predict solvation. For example, Cramer, Truhlar, and coworkers[146] have extended their continuum SMD solvation model to ILs and used it to estimate solvation free energies for a number of solutes in twelve different ILs. The method requires as input several experimental properties of the IL, including dielectric constant, refractive index, surface tension, and acidity and basicity parameters. To our knowledge, this approach has only been applied to examine the solubility of organic species, but has not been applied to examine gas solubility in ILs.

Perhaps the most popular approach for modeling solubility that utilizes a quantum calculation in conjunction with a continuum treatment of the solvent is based on the COnductor-like Screening MOdel (COSMO). Klamt and coworkers[147] were the first to apply the COSMO-RS model in a "real solvent" manner (hence the "RS" suffix) to study the solubility of organic molecules in ILs. Briefly, the method involves carrying out quantum mechanical calculations on individual solutes in a conducting "continuum" which eliminates the need to explicitly model solvent molecules. The resulting geometries and surface charge densities are used to compute the interactions with the solvent (IL) via pairwise interacting surface segments. A statistical thermodynamic approach is then used to estimate solute activity coefficients. Details of the procedure can be found in a review by Diedenhofen and Klamt.[148] The COSMO-RS method is attractive because it is relatively fast and so can be used to virtually screen solubility in ILs for different classes of solutes.

Klamt and coworkers[147] examined the same 38 organic compounds and 3 ILs for which experimental infinite dilution activity coefficient data were available.[74–76] They found that the method gave very good qualitative and, in many cases, quantitative agreement with experiment. Since then, there have been dozens of papers published in which COSMO-RS has been applied to examine solubilities in ILs. Applications involve screening studies to identify the best IL for the extraction of alkenes from alkanes[149,150] and alcohols from water,[151] among other applications. The predictive capability of the COSMO-RS model for 15 gases in 27 ILs was evaluated by Youngs and coworkers.[152] It was found that COSMO-RS can generally provide qualitative predictions of gas solubility, but quantitative results were sometimes lacking. For some systems, even qualitative trends were not captured. This points out the limitations of methods that fail to characterize the specific interactions that are important for solvation.

A variation of the basic COSMO approach (the so-called COSMO-SAC method,[153] where SAC stands for "segment activity coefficient") has been used to screen ILs for possible use as CO_2 capture solvents.[154] A total of 65 cations and 32 anions were examined, forming a total of 2080 distinct ILs. Estimated Henry's Law constants agreed reasonably well with available experimental data. Paduszyński has written an excellent comprehensive review on the use of COSMO-RS for predicting solvation, which we highly recommend.[155]

Atomistic force field methods

Atomistic simulations have also been used extensively to model gas solubility in ILs. This approach treats all the molecular-level interactions explicitly, thereby overcoming some of the limitations of implicit or continuum solvation models. To treat such systems in a computationally efficient manner, an approximate classical representation of the energetics (a "force field") is used. Molecular dynamics or Monte Carlo methods are used to provide statistical sampling of conformations.

The very first attempt at modeling solubility in ILs was carried out using an atomistic force field-based simulation. Lynden-Bell and coworkers[156,157] used molecular dynamics to calculate the interactions and excess chemical potential of water, methanol, dimethyl ether and propane in 1,3-dimethylimidazolium chloride. Because their calculations treated the interactions between the solute and solvent explicitly, they were able to provide molecular-level explanations for some of the solvation trends they observed. For example, they found that the solute hydroxyl groups associated mainly with the chloride anion, and that each water molecule associated with two chloride ions via hydrogen bonding interactions. The ether and alkane did not associate strongly with the anion, and cation arrangement about the solutes was diffuse. This work confirmed the importance of electrostatic interactions and hydrogen bonding on solvation. The detailed information on specific interactions responsible for solvation trends obtained from this method suggested that such techniques could not

only make solvation predictions, but could also provide guidance as to the physical interactions that were most important in determining solubility. Many subsequent atomistic calculations of infinite dilution solubility were carried out using a variety of approaches; in general, these methods agree reasonably well with experimental data.[158–160]

Atomistic simulations enable one to compute not just infinite dilution properties but also full isotherms, which as noted earlier is crucial. Maurer and coworkers were the first to compute an isotherm for a gas in an IL.[161,162] They used isobaric Gibbs ensemble Monte Carlo to estimate the solubility of O_2, CO_2, CO, and H_2 in the IL $[C_4C_1im][PF_6]$. Subsequent work has shown that quantitative results can be obtained for CO_2,[163–165] NH_3,[166] sulfur compounds,[167] and light hydrocarbons.[168] Water poses a particular problem for atomistic simulations; commonly used fixed charge force fields fail to capture experimental absorption isotherms. It is likely that more advanced force fields that treat solute and solvent polarizability are needed.[169] The absorption of gas mixtures can also be readily simulated with these methods[170]; this is a major advantage because mixed gas experiments are significantly more difficult to conduct than pure gas experiments as discussed previously.

These and other studies have demonstrated that the physical solubility of gases in ILs can be modeled accurately using atomistic-level simulations. Force fields for solutes and many ILs are readily available,[171,172] and the steady increase in computing power has meant that the time and expense for performing these calculations continues to decrease. Classical atomistic force field-based methods are the most predictive and accurate approaches for determining macroscopic solubility of gases in ILs, but they are also the most computationally intensive. They enable the estimation of infinite dilution solvation behavior as well as full isotherms. Quantum methods that approximate the solvent as a continuum enable qualitative and in some cases quantitative estimates of solvation free energies and infinite dilution behavior. They are particularly well suited for screening studies where relative solubilities are most important. QSPR methods are fast and effective when a significant amount of experimental data are available. They enable data correlation in terms of a small number of easily determined descriptors.

Advances in predictive methods for gas solubility in ILs will likely not rely on any one method, but will instead leverage computing power advances to develop improved machine learning algorithms, better force fields, and improved simulation algorithms. Computational methods of the kind described here are an important complement to experimental measurements for determining physical solubility of gases in ILs. Treating reactive systems such as the CO_2/acetate anion described earlier or task-specific ILs[173] remains a major challenge for the modeling community and advanced methods are required to model such systems.

Concluding Remarks

A deeper understanding of molecular interactions between gases and ILs is still required. The focus on the solubility of important industrial gases in ILs must now include transport and calorimetric measurements. Only a few articles have been published on diffusion measurements[50,92–94,174–176] and enthalpies of dissolution[105,177] in ILs. Typical diffusion coefficients for CO_2 in imidazolium-based ILs range from 1×10^{-5} to 1×10^{-6} $cm^2\ s^{-1}$ and heats of mixing from a few kJ mol^{-1} (physical sorption) to 30–40 kJ mol^{-1} (chemical sorption).[105] Gas–liquid interfaces are also being studied and experiments have shown interfacial water uptake is much more rapid at the surface than in the bulk.[178] Heat of mixing calculations using EOS models are only semiquantitative; therefore, experimental measurements are needed to develop process simulations and accurate economic models.

Theoretical methods such as QSPR and COSMO-RS have been used to perform screening studies to search for new ILs with certain solvation characteristics, while atomistic simulations and quantum chemical calculations have provided molecular-level details that have greatly enhanced our understanding of solvation in ILs. The reliability and accuracy of these methods is generally good, but the range of systems investigated is still very small. More benchmark studies are needed where experimental measurements and modeling studies are carried out on a range of well-characterized systems. In general, these methods are not able to handle reactive systems (i.e., chemical absorption)[173] in a direct manner, although a number of advances have been made.[179–181]

New materials are also being developed for gas sensors,[182,183] supported IL membranes (SILMs) and poly(IL) membranes,[184–187] carbon capture[188–190] and chemical reaction using supported IL phases (SILPs), where the IL is confined on the surface or in the pores of the material.[191–194] Professor Daniel Armstrong at the University of Texas in Arlington has developed a new class of capillary GC columns with stationary phases based on ILs. His group has synthesized dicationic and polycationic ILs which are stable to water and oxygen even at high temperatures.[195] A variety of capillary GC columns are now available based on IL technology.[196]

In the past couple of years (2015–2016), we have also seen some of the largest scale IL processes announced which require knowledge of gas solubility. First, Queens University Ionic Liquids Laboratory in collaboration with the Malaysian oil and gas company, Petronas, has developed an IL process for the efficient scrubbing of mercury vapor from natural gas.[197,198] The process is now operating on an industrial scale using chlorocuprate (II) ILs impregnated on high surface area porous solid supports. The SILP approach to heterogenize the IL allowed the material to be used in standard industrial-scale mercury removal equipment and the rapid commercialization of the process. The SILP containing IL outperformed the incumbent activated carbon and better manages process upsets such as spikes in mercury concentration.

Chevron announced in October, 2016, the development of a new chloroaluminate IL alkylation process.[199–201] The chloroaluminate ILs provide high activity, selectivity and catalyst stability for C_4 alkylation and provide Chevron with an alternative to using corrosive and toxic hydrofluoric acid as a catalyst.

Molecular-level understanding of the gas-IL interactions is still in progress and should provide future insight into the detailed liquid structure that can guide new experiments. Once an application and IL are identified, several other properties must still be evaluated.[28] First, the cost of the IL and financial benefit must be calculated and clearly provide a value

proposition compared with the incumbent technology. The chemical stability of the IL must be demonstrated in the presence of the gases (and impurities) at operating conditions and required time scales. Materials of construction, corrosion, transport limitations, foaming, toxicity, waste handling, to name a few, are additional details that must also be considered.[28] Traditional unit operations (i.e., columns and tanks) may be employed, but new materials such as SILMs should also be considered. Although IL-based processes share the same hurdles to development and commercialization as any new chemical process, it is our belief that ILs still hold the possibility for future gas separation, chemical reaction, and many other new applications.[202]

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