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Taylor, S. F. R., Brittle, S. A., Desai, P., Jacquemin, J., Hardacre, C., & Zimmerman, W. A. (2017). Factors affecting bubble size in ionic liquids. Physical Chemistry Chemical Physics. DOI: 10.1039/C7CP01725A

Published in:
Physical Chemistry Chemical Physics

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
Link to publication record in Queen's University Belfast Research Portal

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Factors Affecting Bubble Size in Ionic Liquids

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This study reports on understanding the formation of bubbles in ionic liquids (ILs); with a view to utilising ILs more efficiently in gas capture processes. In particular, the impact of the IL structure on the bubble sizes obtained has been determined in order to obtain design principles for the ionic liquids utilised. 11 ILs were used in this study with a range of physico-chemical properties in order to determine parametrically the impact on bubble size due to the liquid properties and chemical moieties present. The results suggest the bubble size observed is dictated by the strength of interaction between the cation and anion of the IL and therefore the mass transport within the system. This bubble size - ILs structure - physical property relationship has been illustrated using a series of QSPR correlations. A predictive model based only on the sigma profiles of the anions and cations has been developed which shows the best correlation without the need to incorporate the physico-chemical properties of the liquids. Depending on the IL selected mean bubble sizes observed were between 56.1 and 766.9 μm demonstrating that microbubbles can be produced in the IL allowing the potential for enhanced mass transport and absorption kinetics in these systems.

1 μm to 999 μm, have advantageous mass transfer properties over larger size bubbles. The rate at which mass transfer can occur is proportional to the interfacial area between which mass transfer is to occur. A reduction in bubble size increases the surface area to volume ratio and, therefore, smaller bubbles are favourable for increased surface area and mass transfer properties.6,5 Previously reported research documenting the use of microbubbles illustrates how these finer bubbles can improve numerous aqueous systems. Processes which have been shown to increase their efficiency through introduction of microbubbles include algal growth, separation rates and mixing in airlift-loop- bioreactors (ALBS).3,6-9 Therefore, the ability to create small bubbles within the IL media would enhance the mass transport and make ILs more applicable for gas capture systems.

In aqueous solutions, it has been shown that the charge density of the ions in solution effects the stabilisation of bubbles,10 a similar trend has also been seen with IL ions in solution.11 However the use of neat IL media will result in a different system with a number of other factors influencing bubble size/stability.

The mass transport properties within ILs is not well studied, to date, and bubble size data is only reported for a small number of ILs with the focus mainly on imidazolium-based ILs.12-16 These reports agree that viscosity and surface tension are the dominating factors in determining the bubble behaviour. In general, bubble size increases as viscosity increases and in cases where IL viscosities are similar, surface tension becomes the governing factor.16 Other experimental conditions have been investigated such as addition of water13, temperature12-16, gas flow rate,12 gas type15 and reactor geometry.15 The effect of the addition of water and the
increase in temperature both result in decreases in bubble diameter potentially due to the subsequent decrease in viscosity. It has been found that mass transport models used for molecular solvents do not fit the data gained from IL systems as the gas-liquid interface is different; cations and anions are both present at the interface with no segregation and cation rings have been found to sit perpendicular rather than parallel to the surface. Other studies have been performed examining the mass transfer properties of CO2 in ILs using a combined computational fluid dynamic (CFD) and population balance model (PBM). However, the study of bubble size distribution within multi bubble systems in many ILs is still largely unreported and, therefore, a comprehensive study of bubble distributions within a wide range of ILs is required if ILs are to be implemented as reaction/separation media at an industrial scale.

This study considers a family of 11 ILs examining the key IL physico-chemical parameters that affect the sizes of bubbles produced within the media. The overall aim of this work is to develop design parameters which allow the IL to facilitate the generation of small bubbles without detrimentally affecting the gas affinity or increasing the energy consumption or process cost. For this reason, several Quantitative Structure-Property-Relationships-based correlations (QSPR) were investigated to illustrate a bubble size - ILs structure – physical properties relationships using key physical properties and/or molecular descriptors.

**Experimental**

**Materials**

Trihexyltetradecylphosphonium bromide [P66614]Br (97 %), Trihexyltetradecylphosphonium chloride [P66614]Cl (98 %), Trihexyltetradecylphosphonium decanoate [P66614][Dec] (97 %) and Trihexyltetradecylphosphonium dicyanamide [P66614][DCA] (97 %) were used as received from Cytec and 1-ethyl-3-methylimidazolium dicyanamide [C4mim][DCA] (98 %), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C4mim][NTf2] (≥97 %), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C4mim][NBF4] (≥98 %) and 1-butyl-3-methyl pyrrolidinium bis(trifluoromethylsulfonyl)imide [C4mpyr][NTf2] (≥98 %) were used as received from Merck. Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide ([P66614][NTf2]) was synthesised by dissolving [P66614]Cl (50.8 g, 0.098 mol) in dichloromethane (100 cm3) and adding this solution dropwise to LiNTf2 (3M, 97 %, 28.7 g, 0.1 mol) dissolved in Milli-Q ultra-pure water (100 cm3). This solution was stirred under ambient conditions overnight. The organic layer was then removed and washed with doubly distilled, deionised water (100 cm3) five times and dried in vacuo. 1-Ethyl-3-methylimidazolium ethylsulfate ([C4mim][EtSO4]) was synthesised by dissolving diethylsulfate (Sigma-Aldrich, 98 %, 154.2 g, 1 mol) in ice cold toluene (Sigma-Aldrich, ≥99.5 %, 100 cm3) and adding this solution dropwise to 1-methylimidazole (Sigma-Aldrich, 99 %, 82.1 g, 1 mol) dissolved in water (500 cm3) in an ice bath under a nitrogen atmosphere. This solution was stirred overnight. The organic solvent was then removed and the former IL was then sequentially washed with toluene (100 cm3) and dried in vacuo five times. 1-Butyl-3-methylimidazolium trifluoroacetate [C4mim][TFA] was synthesised from trifluoroacetic acid (Sigma-Aldrich, 99 %, 114.0 g, 1 mol) added dropwise to 1-butyl-3-methylimidazolium chloride (174.7 g, 1 mol) dissolved in Milli-Q ultra-pure water (500 cm3) in an ice bath and allowed to stir overnight. The solvent was then removed using a rotary evaporator to obtain the IL. All ILs were dried in vacuo (< 10-2 mbar @ 40 °C) for a minimum of 48 h and maintained under a flow of dry N2 overnight before microbubble measurements were carried out. After drying, the water content of the ILs was measured using a Metrohm 787 KF Titrino Karl Fischer as < 0.1 wt% for all ILs. The purity of the synthesized ILs was analysed using 1H NMR using a Bruker 300 MHz Ultra shield Plus NMR spectrometer and the results were consistent with literature reports.

**Methods**

Nitrogen (BOC, 99.998 %) was delivered to the IL via a Bronkhorst mass flow controller. The gas was flowed for ~ 5 min prior to the measurements being made in order to equilibrate the pressure within the system, including the ceramic porous material. During this time bubbles continuously detached from the surface of the ceramic and into the IL. The ceramic porous material used in this study has an average pore size of 2.5 µm as shown in Figure 1. Scanning electron microscopy (SEM) was carried out on a JEOL JSM 6300 SEM with an Agar MB7240 gold sputter coater. This material has a thickness of 10 mm and the pressure required to allow bubbling in an aqueous system is 2.4 bar (gauge) at 298 K and 101.325 kPa.

Typically, the microbubble rigs reported previously have volumes of > 50 L8; however, due to the use of ILs and the associated synthesis and procument costs, the equipment was scaled down to allow the use of smaller volumes. In these measurements, ~120 cm3 of IL was employed. The rig, consists of a stainless-steel base with an inlet chamber and a microporous ceramic diffuser. The chamber section is secured to a quartz glass viewing section for bubble visualisation and imaging. Nitrogen is bubbled into the IL at 3 cm3 min-1 for each of the ILs in order to directly compare the bubble size.
distribution in each case. This particularly low flow rate is used to minimise the amount of bubbles created within the IL and, therefore, reduce the risk of overlapping bubbles during imaging. In addition, all materials of construction were tested to examine the effect of the ILs to ensure compatibility with the IL media.

**Contact angle measurements.** Young’s equation (1) was used to determine the contact angle (θ) utilising the surface tensions of the three phases present in the system:

\[
\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{SV}}
\]  

(1)

where γ is the surface tension at the interface of two phases and S, V and L represent the solid, vapour and liquid phases, respectively.

This relationship suggests that the contact angle is independent of drop size, provided that the drop is small enough to ignore gravitational effects.\(^{21}\)

The contact angle reported, herein, is the angle that a droplet of IL makes when it is placed on a ceramic surface. It is measured at 293.15 K and 101.325 kPa using an Attension Theta tensiometer, which is able to measure contact angles using its optimised setup including a monochromatic light source, adjustable sample holder and dedicated software. This allows a droplet of IL placed on a non-porous ceramic substrate to be analysed and its volume and contact angle easily measured. The ceramic substrate material was chosen to replicate that of the porous ceramic diffuser of the microwbubbling rig without the complications of a porous structure. The IL was pipetted onto a cleaned substrate stage. The ceramic substrates were cleaned by applying chloroform then propan-2-ol then water followed by the propan-2-ol then chloroform before drying. Three measurements were taken and an average value taken providing a standard deviation of 2° sigma.

Prior to both bubble imaging and contact angle experiments the ILs were dried/equilibrated with the gas stream by bubbling nitrogen through the media overnight at room temperature and stored within a vacuum desiccator.

**Bubble size measurements.** Bubbles of nitrogen in the ILs were imaged using an optical method utilising a digital camera (Pixelink PL742, 1.3 MP enclosed camera with a 2/3” On Semi IBIS 5B sensor and 27 fps output). The sensor features a 6.7 µm pixel pitch and is capable of 10-bit output) and associated software. The IL was backlit using a ThorLabs White LED Array light source (LIU004) with an intensity of 1700 µW/cm\(^2\) and emitted at a peak of 450 nm. The bright LED light source, focused using a lens, is diffused into a more uniform light using a white plastic translucent optical diffuser layer, before entering the bubble visualisation rig. The rig was constructed using transparent quartz glass which was tested previously and known to be compatible with the ILs. This setup is shown in Figure 2.

Once the images of bubbles in the IL have been taken, the bubble size distribution was obtained using bespoke bubble-sizing software (Figure 3).\(^{22}\) This software is able to automate a number of imaging processing techniques on a large number of images, each containing multiple bubbles.
where $s$ is the standard deviation of sample, $n$ is the total number of bubbles, $x_i$ is sample bubble size and $D[1,0]$ is the mean bubble size.

**COSMOTHERMX calculations.** The COSMOTHERM software is based on the Conductor-like Screening Model for Real Solvent method (COSMO-RS), which combines statistical thermodynamics with the electrostatic theory of locally interacting molecular surface descriptors.$^{23}$

Prior to utilisation of this software, the structure of each ion involved was optimized within the Turbomole 7.0 program package,$^{24}$ with a convergence criterion of $10^{-8}$ Hartree in the gas phase DFT calculations combining the Resolution of Identity (RI) approximation$^{25}$ utilizing the B3LYP functional with the def-TZVP basis set.$^{26}$ Each resultant optimized structure was then used as an input for the generation of the most stable conformer of each species using the COSMOCOFX program (version 4.0). The COSMOTHERM software (version C30_1602) was then used to determine the sigma profile, COSMO volume of each ion, as well as, the free volume in each selected IL by following the same methodology as already presented previously by our group.$^{27}$ Additionally, sigma-moments were determined to further analyse the capability of the COSMOTHERM software to be used as a QSPR-based approach to correlate average IL bubble sizes as the function of the ILs structure by following the same approach as that reported by Klamt et al.$^{23}$

**Results and discussion**

The series of ILs were selected for microbubble testing to cover a wide range of viscosities (16-2900 mPa·s), densities (0.8-1.5 g·cm$^{-3}$), molecular weights (170-760 g·mol$^{-1}$) and hydrophobicity as measured by contact angle (11.7°-56.4°) at 293.15 K and 101325 Pa. The structures of the cations and anions of the various ILs used are given in Figure 4.

In this study, the bubble size data have been acquired after bubbling with nitrogen to understand how the various IL properties correlate with the bubble size observed. Nitrogen gas was used instead of CO$_2$ to limit the effect of gas dissolved in selected ILs on the bubble size distributions observed as it is very well reported in the literature that N$_2$ has a lower solubility than CO$_2$ in several ILs.$^{28,29}$ The results from the microbubble experiments are given in Table 1; including average bubble size and measures of distributions (standard deviation and kurtosis).

Table 1 shows, in general, that the ILs containing a tetraalkyl phosphonium cation exhibited the largest bubble sizes whereas the imidazolium based ILs resulted in the smallest bubble sizes observed. The lowest mean bubble size was observed in [C$_2$ mim][DCA] and the largest mean bubble size was observed in [P$_{66614}$]Cl. To help understand the cause of the differing bubble size distributions and average bubble sizes in a selection of ILs, individual properties (viscosity, density, contact angle, molecular weight and free volume) are considered and are also listed in Table 1.

From an initial inspection of bubble size results and IL parameters (Table 1) is a previous work, it was

![Figure 4. IL anions and cations molecular structures.](Image)

| Molecular weight (g·mol$^{-1}$) | Viscosity (Pa·s) | Density (kg·m$^{-3}$) | Contact angle (°) | Free volume (cm$^3$·mol$^{-1}$) | Mean bubble radius (μm) | Standard deviation (μm) | Kurtosis |
|-------------------------------|-----------------|----------------------|------------------|-------------------------------|------------------------|------------------------|----------|
| [C$_2$ mim][DCA]              | 177.2           | 0.0161$^{30}$        | 1104.0$^{30}$    | 43.7                          | 19.96                  | 56.1                   | 29.3     | 5.03    |
| [C$_2$ mim][TFA]              | 252.2           | 0.0769$^{31}$        | 1215.5$^{31}$    | 35.3                          | 23.51                  | 62.9                   | 32.9     | 8.56    |
| [C$_2$ mim][EtSO$_3$]         | 236.3           | 0.0976$^{32}$        | 1238.8$^{32}$    | 53.5                          | 21.76                  | 102.0                  | 52.3     | 3.72    |
| [P$_{66614}$][DCA]            | 549.9           | 0.3630$^{33}$        | 897.6$^{33}$     | 25.2                          | 134.42                 | 270.9                  | 109.6    | 0.10    |
| [C$_2$ mim][NTf$_2$]          | 419.4           | 0.0507$^{34}$        | 1436.6$^{34}$    | 36.7                          | 31.93                  | 276.9                  | 109.5    | -0.02   |
| [C$_2$ mim][NTf$_2$]          | 391.3           | 0.0325$^{35}$        | 1518.7$^{35}$    | 56.4                          | 24.82                  | 279.4                  | 69.7     | 1.51    |
| [Campyr][NTf$_2$]             | 422.4           | 0.0776$^{36}$        | 1394.9$^{36}$    | 27.3                          | 35.36                  | 400.6                  | 205.6    | -0.43   |
| [P$_{66614}$][NTf$_2$]        | 764.0           | 0.3367$^{37}$        | 1066.1$^{37}$    | 20.9                          | 140.25                 | 415.4                  | 168.7    | 0.44    |
| [P$_{66614}$][Dec]            | 655.1           | 0.4715$^{38}$        | 880.6$^{38}$     | 18.5                          | 167.90                 | 517.7                  | 150.3    | 1.79    |
| [P$_{66614}$][Br]             | 563.8           | 2.9884$^{39}$        | 955.2$^{39}$     | 21.6                          | 119.19                 | 582.1                  | 334.6    | -0.64   |
| [P$_{66614}$][Cl]             | 519.3           | 2.7291$^{37}$        | 889.9$^{37}$     | 11.7                          | 125.39                 | 766.9                  | 349.7    | -0.01   |
expected that the viscosity would be a significant factor in determining the bubble size with an expected trend of increased bubble size with increased viscosity. The dependence of bubble size with respect to the ILs viscosity is given in Figure 5.

Figure 5 shows the expected general trend that with increased viscosity (η) larger average bubble radii are found. Equation (4) was then used to correlate this data set within a R² value close to 0.70.

\[
\text{Mean bubble size} = 526.1 + 109.7 \cdot \ln(\eta) \quad (4)
\]

where the mean bubble size and the viscosity are given in μm and Pa·s, respectively.

However, the six ILs with the lowest viscosities ([C₄mim][DCA], [C₄mim][EtSO₄], [C₄mim][NTf₂], [C₄mim][NTf₂], [C₄mim][TFA] and [C₅mpyr][NTf₂]) have viscosities within a similar range (0.0161-0.0976 Pa·s) but produce very different average bubble sizes differing by up to 500% from 56.1 μm to 279.4 μm. In particular, [C₅mpyr][NTf₂] which has a viscosity of 0.0776 Pa·s gives an average bubble size of 400.6 μm and [C₄mim][TFA] which has a similar viscosity of 0.0769 Pa·s results in a much lower average bubble size of 62.9 μm. This clearly shows that there are other factors apart from viscosity that affect the ILs bubble size distribution.

Wettability (contact angle) has also been reported previously as a contributing factor in determining the bubble size. It has been shown that bubble sizes increase with increasing contact angle; however, this was demonstrated using water as the liquid and the hydrophobicity of the surface was modified to produce a range of contact angles and the resulting bubble size measured. Figure 6 shows the average bubble radius against contact angle for each IL studied. In all cases, the surface remained constant and the hydrophobicity of the liquid is varied. In contrast to the previous observations, in general, the bubble size was found to decrease with increasing contact angle which could be correlated reasonably (R² = 0.77) using the following equation:

\[
\text{Mean bubble size} = 1395.6 \cdot \exp(-0.0522 \cdot \gamma) \quad (5)
\]

where the mean bubble size and the contact angle are given in μm and °, respectively.

However, as observed with the trends with viscosity, ILs with similar contact angles resulted in significantly different bubble sizes. For example [C₄mim][TFA] and [C₄mim][NTf₂] have very similar contact angles (35.3 and 36.7 °, respectively) but produce bubbles with an average size of 62.9 and 276.9 μm, respectively. This clearly demonstrates again that there are other factors apart from viscosity and contact angle that could affect the ILs mean bubble size distribution.

The relationship of mean bubble size against molecular weight (MW) is plotted in Figure 7. In general, the lower the molecular weight of the IL the smaller the bubble size formed. This tendency may be represented by a straight line (R² = 0.51) which follows the equation below:

\[
\text{Mean bubble size} = 0.7717 \cdot \text{MW} \quad (6)
\]
where the mean bubble size and the molecular weight are given in µm and in g·mol⁻¹, respectively. Again, although [P66614]Cl and [P66614][DCA] have similar molecular weights (519.3 and 549.9 g·mol⁻¹, respectively) different bubble sizes (766.9 and 270.9 µm, respectively) are observed. Figure 8 shows the relationship between ILs density and mean bubble size. In this case, no significant correlation was observed. Figure 9 shows the trend of the bubble size with respect to the free volume of each IL determined using COSMOthermX. To obtain the free volume, the total COSMO volume of each IL was calculated by the sum of the COSMO volumes of the anion and the cation directly determined by COSMOthermX. An estimation of each IL free volume (see Table 1) is then calculated by taking the difference between the calculated molar volume and the COSMO volume of the IL by following the same approach as that reported previously. As shown in Figure 9 a general trend in bubble size as the function of the IL free volume is observed. As the free volume (\( f_v \)) of the IL increases a larger average bubble size is observed. This overall trend was then fitted by a straight line (\( R^2 = 0.38 \)) which follows the equation below:

\[
\text{Mean bubble size} = 3.8125 \cdot f_v \quad (7)
\]

where the mean bubble size and the free volume are given in µm and in cm³·mol⁻¹, respectively.

Whilst there is a general trend the correlation is poor and is only qualitative. For example, [P66614]Cl and [P66614][DCA] have similar molar volumes (583.6 and 612.6 cm³·mol⁻¹, respectively) and free volumes (125.4 and 134.4 cm³·mol⁻¹, respectively) but give very different average bubble sizes (766.9 and 270.9 µm, respectively). Correlation of the bubble size data to physico-chemical properties of each IL shows that no individual physical property is the determining factor and that a combination of the properties influences the results. However, notably contact angle and viscosity have the strongest correlation to the mean bubble size in ILs. To further analyse this behaviour, a simple QSPR was setup to correlate the mean bubble size as the function of these key properties as follows:

\[
\begin{align*}
Y_{\text{exp}} &= a \cdot \eta + b \cdot \gamma + c \cdot MW + d \cdot f_v \\
Y_{\text{corr}} &= Y_{\text{exp}} - \text{Relative Absolute Deviation (RAD)}
\end{align*}
\]

where \( a, b, c \) and \( d \) are the QSPR type fitting parameters reported in Table 2, the mean bubble size, the viscosity, contact angle, molecular weight and free volume are given in µm, Pa·s, °, g·mol⁻¹ and cm³·mol⁻¹, respectively.

As reported in the Eq. 8 the QSPR constant was set as equal to zero as it was assumed that no bubble could be formed in the absence of the IL. By following this methodology, a reasonably good QSPR correlation (equation \( y = x \) with a \( R^2 = 0.85 \), RAAD = 26 %) was found between these properties and the experimental mean bubble size data as shown in Figure 10. This further demonstrates the impact of highlighted properties on the mean bubble size in selected ILs. As shown in Table 2

\[
\begin{align*}
\text{Table 2: QSPR-type fitting parameters of the Eq. 8 and comparison between experimental and correlated mean bubble sizes.}
\end{align*}
\]

| A   | b      | c      | d      | Mean bubble radius (µm) | RAD (%) | Experimental | Correlated |
|-----|--------|--------|--------|--------------------------|---------|--------------|------------|
| +125.6 | -1.749 | +0.8894 | -1.175 |                          |         |              |            |

\[
\text{RAD (%)} = 100 \cdot \frac{\left| Y_{\text{exp}} - Y_{\text{corr}} \right|}{Y_{\text{exp}}} \quad (9)
\]

where \( Y_{\text{exp}} \) and \( Y_{\text{corr}} \) represent the experimental and correlated mean bubble sizes, respectively.
and as expected from Figures 5 and 7, the molecular weight and the viscosity positively contribute to the size of the bubble in IL a contrario of the contact angle (expected from Figure 6) and more surprisingly the free volume (unexpected from Figure 9) as both properties have a negative QSPR fitting parameter (parameters b and d).

A further analysis of the number of properties and fitting parameters was then conducted to verify the impact of each property on the QSPR performance. In this case, each of the parameters a, b, c and d was set to zero and the significance of its effect evaluated. As exemplified in Figure S12 along with parameters and calculated data reported in Table S1 - ESI, by neglecting the IL free volume (parameter d = 0 in Eq. 8) a poor QSPR correlation was found (y = 1.767 x with a R² = 0.53, RAAD = 53 %), demonstrating the importance of this property on the QSPR correlation performance. This could be attributed to two main factors: (i) the free volume is a key property describing the mean bubble size in ILs; and/or (ii) the increase of the fitting parameters in Eq. 8 enhances the QSPR correlation. However, differences observed from parity plots between experimental vs. calculated mean bubble size by excluding (Figure S12, slope = 1.767) or including (Figure 10, slope = 1) the free volume into the QSPR correlation clearly show its impact on the slope of the straight line, and in fact on the quality of the QSPR correlation. However, even if a good correlation was observed by using all highlighted physical properties, by analysing data reported in Table 2, it appears that this QSPR is unable to provide the correct mean bubble size trend as the function of the IL structure as experimentally it was found that mean bubble size increases in the following order: [C₅mim][DCA] < [C₅mim][TFA] < [C₅mim][EtSO₄] < [P₆₆₆₄][DCA] ~ [C₅mim][NTf₂] ~ [C₅mim][NTf₂] < [C₅mim][NTf₂] < [C₅mim][NTf₂] < [P₆₆₆₄][Dec] < [P₆₆₆₄][Br] < [P₆₆₆₄][Cl] whereas the QSPR gives the following trend: [C₅mim][DCA] < [C₅mim][TFA] < [C₅mim][EtSO₄] < [C₅mim][NTf₂] ~ [C₅mim][NTf₂] < [C₅mim][NTf₂] < [C₅mim][NTf₂] < [P₆₆₆₄][DCA] < [P₆₆₆₄][Dec] < [P₆₆₆₄][Br] together with a Relative Absolute Average Deviation (RAAD) close to 26 %. Therefore, the ability for the bubbles to form in the IL was evaluated by examining the strength of the cation and anion interaction, as well as correlating the trends with respect to the shape of the distribution (Figures S1-S11 – ESI).

In order to provide some quantification of the interactions present, sigma profiles were calculated for each of the IL cations and anions and were summarised in Tables 3 and 4. Figures S1-S3 show the bubble size distributions observed for [C₅mim][DCA], [C₅mim][EtSO₄] and [C₅mim][NTf₂] respectively, in this data set the cation remains constant which shows the

![Figure 10](image)

**Figure 10.** Parity plot between the experimental and correlated mean bubble size using Eq. 8 along with parameters reported in Table 2.

| Structure and abbreviation | Cosmo Volume (Å³) | Structure and abbreviation | Cosmo Volume (Å³) |
|---------------------------|-------------------|---------------------------|-------------------|
| Cl                        | 36.0874           | Br                         | 42.2134           |
| [DCA]                     | 82.5478           | [TFA]                      | 95.7199           |
| [EtSO₄]                   | 125.2487          | [NTf₂]                     | 219.6735          |
| [Dec]                     | 247.3144          | [C₅mim]+                   | 154.1699          |
| [C₅mim]+                  | 155.7999          | [C₅mim]+                   | 215.1805          |
| [P₆₆₆₄]+                  | 749.6190          |                            |                   |
effect changing the anion. The mean bubble sizes observed for these three ILs are 56.1, 102.0 and 279.4 µm for [C2mim][DCA], [C2mim][EtSO4] and [C2mim][NTf2], respectively. This trend is also found for the width of the bubble size distribution with the ILs based on [DCA] < [EtSO4] < [NTf2]; as described by the standard deviation measuring 29.3, 52.3 and 69.7 µm, respectively. This quantitatively shows that as the standard deviation decreases the distributions become narrower. A similar trend is also found for the kurtosis values for [C2mim][DCA], [C2mim][EtSO4] and [C2mim][NTf2] with values of 5.03, 3.72 and 1.51, respectively, again confirming the order of the size of the distribution widths. These trends may reflect the strengthening of the anion-cation binding. [DCA]: is the smallest anion of the set (82.5478 Å³), its sigma surface shows the charge is mainly located on the three nitrogens within the molecule separated by the two carbons. The sigma profile shows two peaks one representing the polarization charge on the surface of the carbon between 0 and 0.01 e.Å⁻² and a larger second peak at 0.01-0.02 e.Å⁻² for the charge on the nitrogens. As expected, the sigma profile shows that all of the polarization charge is positive which results in a good interaction with the cation. The charge is localised at uniform places within the molecule and, therefore, has strong Coulombic and hydrogen bonding interactions, the latter with the ring hydrogens of the cation. A weaker interaction is found for [EtSO4] due to its increased size (125.2487 Å³), its sigma surface shows that the charge is mainly located on the -OSO₂ group and its sigma profile shows two peaks, one for the alkyl chain of the anion -0.005 to 0.01 e.Å⁻² and one for the OSO₂ section at 0.01-0.02 e.Å⁻². The presence of the ethyl group suggests the contribution of the van der Waals interactions to the cohesive energy inducing weaker interaction between the [EtSO4] and the [C2mim]⁺ than those expected with the [DCA]⁻ anion, for example. The weakest interaction is observed for the [NTf2]⁻ due to its larger volume (219.6735 Å³), its sigma surface shows that the charge is less concentrated and spread over a large area of the anion. The sigma profile shows a large region of the charge densities around zero which represents van der Waals type interactions (-0.01 and +0.01 e.Å⁻²), therefore, there is a reduction in the interaction of the anion and cation due to the charge delocalisation and increased sterics. This trend shows that a stronger interaction between the ions leads to a more structured IL and results in a narrower bubble size distribution. Bubble size distributions for [C2mim][NTf2] and [C2mim][TFA] (Figures S4 and S5) are also consistent with this trend. On changing the anion from [NTf2]⁻ to [TFA]⁻ while maintaining [C2mim]⁺ as the cation, a decrease in the mean bubble size from 276.9 to 62.9 µm is observed which is in line with the stronger cation-anion interaction expected for ILs based on the smaller [TFA]⁻ anion (95.7199 Å³) compared with the larger [NTf2]⁻ anion (219.6735 Å³). The sigma profile for [TFA]⁻ also shows two regions of charge for -CF₃ (0 to 0.01 e.Å⁻²) and -COO⁻ (0.01 to 0.02 e.Å⁻²). The small size of the molecule and the positive polarisation charge will result in good packing and strong interactions of cation and anion. [C2mim][TFA] and [C2mim][DCA] also have the smallest mean bubble sizes for all the ILs studied with the narrowest bubble size distribution and most uniform bubbles as illustrated by the two largest kurtosis values (8.56 and 5.03). Figures S3, S4, S10 and S11 show the bubble size distributions observed for [C2mim][NTf2], [C2mim][NTf2], [P66614][NTf2] and [C2mim][NTf2], respectively, which shows the effect of changing the cation. The mean bubble sizes observed for [C2mim][NTf2], [C2mim][NTf2],

Table 4. Sigma profile evaluated by COSMOthermX for each selected ion

| Ion     | Sigma profile |
|---------|---------------|
| Cl      |                |
| Br      |                |
| [DCA]   |                |
| [TFA]   |                |
| [EtSO4] |                |
| [NTf2]  |                |
| [Dec]   |                |
| [C2mim]⁺|                |
| [C2mim]⁺|                |
| [C2mim]⁺|                |
| [C2mim]⁺|                |
| [C2mim]⁺|                |
| [C2mim]⁺|                |

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[P66614][NTf2] and [Cmpyr][NTf2] are 279.4, 276.9, 400.6 and 415.4 µm respectively. Therefore, the mean bubble size trend is in the order [Cmim]+ < [Cmpyr]+ < [Cmpyr]1 < [Cmim]+ < [P66614]+. The standard deviations of [Cmim][NTf2], [Cmpyr][NTf2], [Cmpyr][NTf2] and [P66614][NTf2] are 69.7, 109.5, 205.6 and 168.7 µm, respectively. Comparable values are observed for [Cmim][NTf2] and [Cmpyr][NTf2] as the two cation structures are very similar. Table 3 shows similar COSMO volumes of 154.1699 Å3 and 155.7999 Å3 for [Cmim][NTf2] and [Cmpyr][NTf2], respectively. Furthermore, from their sigma surface it is seen that, in both cases, the positive charge is located on the carbon between the two nitrogens but also delocalised around the aromatic ring. Table 4 shows almost identical sigma profiles for the two imidazolium cations this is expected as previous reports have shown that non-polar domains are only observed above C6. Therefore, the cation-anion interaction will also be similar resulting in a similar average bubble size value and distributions. The increase in mean bubble size and standard deviation when [Cmim]+ is compared to [Cmpyr]+ is due to the increased size of [Cmpyr]+ (215.1805 Å3), a loss of the n−π interaction and a shift in the polarisation of the charge to indicate the presence of van der Waals interactions which results in a weaker interaction of the [NTf2]: with [Cmpyr]+ compared with [Cmim]+.

In the case of [P66614]+, a further increase in COSMO volume is observed (749.6190 Å3). The sigma surface (Table 3) shows localisation of the positive charge around the phosphorous and the sigma profile (Table 4) shows a larger proportion of the charge density is shifted to positive charge polarisation which is representative of the bulky alkyl groups and resulting van der Waals forces. The weak interaction of the bulky alkyl groups and the large size of the cation results in the larger mean bubble size and wide bubble size distribution. The kurtosis values measured for [Cmim][NTf2] and [P66614][NTf2], are 1.51, and 0.44, respectively, further outlining the reduction in the interaction of the ions when the cation is changed from [Cmim]+ to [P66614]+. It should be noted that the kurtosis values calculated for [Cmim][NTf2] and [Cmpyr][NTf2] do not represent the data correctly due to the presence of a bimodal distribution.

Figures S6-S10 show the bubble size distributions observed for [P66614][Br], [P66614][Cl], [P66614][DCA], [P66614][Dec] and [P66614][NTf2], respectively. The mean bubble sizes measured for [P66614][Br], [P66614][Cl], [P66614][DCA], [P66614][Dec] and [P66614][NTf2] are 582.1, 766.9, 270.9, 517.7 and 415.4 µm, respectively. It is clear that the bubbles created in the [P66614]+ surrounding the aromatic ring. Table 4 shows similar COSMO volumes of 154.1699 Å3 and 155.7999 Å3 for [Cmim][NTf2] and [Cmpyr][NTf2], respectively. Furthermore, from their sigma surface it is seen that, in both cases, the positive charge is located on the carbon between the two nitrogens but also delocalised around the aromatic ring. Table 4 shows almost identical sigma profiles for the two imidazolium cations this is expected as previous reports have shown that non-polar domains are only observed above C6. Therefore, the cation-anion interaction will also be similar resulting in a similar average bubble size value and distributions. The increase in mean bubble size and standard deviation when [Cmim]+ is compared to [Cmpyr]+ is due to the increased size of [Cmpyr]+ (215.1805 Å3), a loss of the n−π interaction and a shift in the polarisation of the charge to indicate the presence of van der Waals interactions which results in a weaker interaction of the [NTf2]: with [Cmpyr]+ compared with [Cmim]+.

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expected given the relative size of the bubbles formed and the void space within the IL. To assess the ability of the sigma profile to describe the mean bubble size distribution of the selected ILs, a second QSPR approach was developed by splitting the polarization charge into 6 regions (region 1: from -0.030 to -0.021 e Å²; region 2: from -0.020 to -0.011 e Å²; region 3: from -0.010 to 0 e Å²; region 4: from 0 to 0.010 e Å²; region 5: from 0.011 to 0.020 e Å² and region 6: from 0.021 to 0.030 e Å²) by calculating the overall populations of charge present on the surface of each ion for each of them. For each region, the overall population of charge of the selected ILs was then determined as the sum of the charges found for its anion and cation as reported in Table S2 – ESI. Then, the following equation was used to set the QSPR model:

$$
\text{Mean bubble size} = e \cdot \text{region 2} + f \cdot \text{region 3} + g \cdot \text{region 4} + h \cdot \text{region 5} + i \cdot \text{region 6}
$$

where e, f, g, h and i are the QSPR type fitting parameters reported in Table 5, the mean bubble size and regions are given in µm and Å², respectively.

From the sigma profiles reported in Table 4, it appears that, for all investigated ions no population of charge was found in region 1, explaining why this descriptor was neglected in Eq. 10. By regressing the experimental mean bubble size distribution using Eq. 10 qualitative correlation (ρ = x, R² = 0.58, RAAD = 56 %) was found as shown in Figure 11 and Table 5 which reflects the importance of hydrogen bonding acceptor (region 2) and donor sites (region 6) to form smaller bubbles in the ILs. However, even if the number of fitting parameters increases by using this second QSPR method rather than initial one (Eq. 8), a lower RAAD was in fact observed (56 % compared with 26 %). Furthermore, as also observed using the Eq. 8 the wrong variation of the mean bubble size with the respect to ILs structure was observed using this second approach as the

$$
\text{Corr. Mean Bubble Size (µm)} = a + b \cdot \text{Mean bubble size (µm)}
$$

Table 5. QSPR-type fitting parameters of the Eq. 10 and comparison between experimental and correlated mean bubble sizes.

|      | e    | f    | g    | h    | i    |
|------|------|------|------|------|------|
| [C₄mim][DCA] | 1.146 | 3.078 | 11.33 | 2.956 | 205.0 |
| [C₄mim][NTf₂] | 1.146 | 3.078 | 11.33 | 2.956 | 205.0 |
| [C₄mim][DCA] | 1.146 | 3.078 | 11.33 | 2.956 | 205.0 |
| [C₄mim][NTf₂] | 1.146 | 3.078 | 11.33 | 2.956 | 205.0 |
| [C₄mim][DCA] | 1.146 | 3.078 | 11.33 | 2.956 | 205.0 |
| [C₄mim][NTf₂] | 1.146 | 3.078 | 11.33 | 2.956 | 205.0 |
| [C₄mim][DCA] | 1.146 | 3.078 | 11.33 | 2.956 | 205.0 |
| [C₄mim][NTf₂] | 1.146 | 3.078 | 11.33 | 2.956 | 205.0 |
| [C₄mim][DCA] | 1.146 | 3.078 | 11.33 | 2.956 | 205.0 |
| [C₄mim][NTf₂] | 1.146 | 3.078 | 11.33 | 2.956 | 205.0 |
| [C₄mim][DCA] | 1.146 | 3.078 | 11.33 | 2.956 | 205.0 |
| [C₄mim][NTf₂] | 1.146 | 3.078 | 11.33 | 2.956 | 205.0 |
| [C₄mim][DCA] | 1.146 | 3.078 | 11.33 | 2.956 | 205.0 |
| [C₄mim][NTf₂] | 1.146 | 3.078 | 11.33 | 2.956 | 205.0 |

Table 6. QSPR-type fitting parameters combining the Eqs. 8 and 10 and comparison between experimental and correlated mean bubble sizes.

|      | a   | b   | c   | d   | e   | f   | g   | h   | i   |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| [C₄mim][DCA] | 56.1 | 82.6 | 47  | 0   | 0   | 0   | 0   | 0   | 0   |
| [C₄mim][TFA]  | 62.9 | 105.0 | 67  | 0   | 0   | 0   | 0   | 0   | 0   |
| [C₄mim][EtSO₂] | 102.0 | 87.4 | 14  | 270.9 | 263.1 | 2.9 |
| [P₅BM][DCA]  | 270.9 | 523.2 | 93  | 270.9 | 263.1 | 2.9 |
| [C₄mim][NTf₂]  | 276.9 | 186.0 | 33  | 276.9 | 279.8 | 1.1 |
| [C₄mim][NTf₂]  | 279.4 | 164.4 | 41  | 279.4 | 279.8 | 1.1 |
| [C₄mim][NTf₂]  | 400.6 | 272.4 | 32  | 400.6 | 272.4 | 32  |
| [C₄mim][NTf₂]  | 415.4 | 551.1 | 33  | 415.4 | 551.1 | 33  |
| [C₄mim][NTf₂]  | 517.7 | 510.7 | 14  | 517.7 | 512.9 | 0.9  |
| [C₄mim][NTf₂]  | 582.1 | 513.5 | 12  | 582.1 | 711.6 | 22  |
| [C₄mim][NTf₂]  | 766.9 | 498.1 | 35  | 766.9 | 622.9 | 19  |

* Relative Absolute Deviation (RAD) calculated using Eq. 9
moments, while the coefficients $C_3$ to $C_6$ are the QSPR fitting parameters. The sigma moments of investigated ILs were then computed as the sum of the sigma moments of the cation and anion as reported in Table S5 – ESI. However, in our present case, in order to avoid over-parameterisation due to the limited number of experimental data points available, the multilinear regression had to be performed with a much lower number of descriptors than those reported in Eq. 11.

According to Klamt et al., the molecular surface area $A$, the second and third sigma moments $M_2^\alpha$, (i.e. electrostatic interaction energy) and $M_3^\alpha$ (i.e. the kind of skewness of the sigma profile), as well as, the third hydrogen bonding acceptor and donor moments $M_{HBacc i}^a$ (i.e. representing the hydrogen bond acidity) and $M_{HBdon i}^a$ (i.e. representing the hydrogen bond basicity) are the five most significant descriptors to be

Table 7. QSPR-type fitting parameters of the Eq. 12 and comparison between experimental and correlated mean bubble sizes.

| |  
|---|---|---|---|
| $C_D$ | $C_i$ | $C_j$ | $C_k$ |
| 1.5865 | +17.321 | +35.234 | -11.359 |
| $C_7$ | $C_8$ | $C_{11}$ | $C_{14}$ |
| -22542 | +136.272 | +75645 | +2307.8 |

where $A^\alpha$ and $M^\alpha$ are the molecular surface area and the $i^{th}$ sigma moment of the species $X_i$, respectively. $M_{HBacc i}^a$ and $M_{HBdon i}^a$ are its $i^{th}$ hydrogen bonding acceptor and donor

| Name | Mean bubble radius ($\mu$m) | RAD $^a$ | % |
|------|-----------------------------|---------|---|
| $[\text{C}i\text{mim}][\text{DCA}]$ | 56.1 | 50.9 | 9.2 |
| $[\text{C}i\text{mim}][\text{TFA}]$ | 62.9 | 97.3 | 55 |
| $[\text{C}i\text{mim}][\text{EtSO}_4]$ | 102.0 | 128.7 | 26 |
| $[\text{P}os\text{sa}][\text{DCA}]$ | 270.9 | 268.1 | 1.0 |
| $[\text{C}i\text{mim}][\text{NTf}_2]$ | 276.9 | 258.9 | 6.5 |
| $[\text{C}i\text{mim}][\text{NTf}_2]$ | 279.4 | 241.6 | 14 |
| $[\text{C}i\text{mpy}][\text{NTf}_2]$ | 400.6 | 400.1 | 0.1 |
| $[\text{P}os\text{sa}][\text{NTf}_2]$ | 415.4 | 458.8 | 10 |
| $[\text{P}os\text{sa}][\text{Dec}]$ | 517.7 | 507.8 | 1.9 |
| $[\text{P}os\text{sa}][\text{Br}]$ | 582.1 | 518.1 | 11 |
| $[\text{P}os\text{sa}][\text{Cl}]$ | 766.9 | 800.0 | 4.3 |

$^a$ Relative Absolute Deviation (RAD) calculated using Eq. 9

Figure 12. Parity plot between the experimental and correlated mean bubble size by combining Eqs. 8 and 10 along with parameters reported in Table 6.

Figure 13. Parity plot between the experimental and correlated mean bubble size by using Eq. 12 along with parameters reported in Table 7.
used for sigma moment QSPR applications. These five parameters were in fact used by default during our parametrisation by keeping the constant as equal to zero for the same reason as stated above. Equation 11 was then set to minimise the number of descriptors to provide the best correlation performance.

In the light of this multilinear regression analysis of our experimental data, this COSMO moment approach, using only the number of parameters representative of the structure of the IL, provides the best correlation, as shown in Figure 13 and Table 7, with $y = x$, $R^2 = 0.98$ and RAAD = 13%.

\[
\text{Mean bubble size} = C_0 \cdot A^2 + C_2 \cdot M_2^1 + C_4 \cdot M_4^1 + C_7 \cdot M_7^1 + C_{14} \cdot M_{14}^1 \]

(12)

As reported in Table 7, the variation of the mean bubble size with respect to the ILs structure seems to be correctly evaluated by using this fourth approach as the mean bubble size follows this order: [C$_2$ mim][DCA] \(<\) [C$_4$ mim][TFA] \(<\) [C$_6$ mim][ETSO$_4$] \(<\) [C$_8$ mim][NTf$_2$] \(<\) [C$_{14}$ mim][NTf$_2$] \(<\) [P$_{66614}$][DCA] \(<\) [C$_{mpyr}$][NTf$_2$] \(<\) [P$_{66614}$][NTf$_2$] \(<\) [P$_{66614}$][Dec] \(<\) [P$_{66614}$][Br] \(<\) [P$_{66614}$][Cl]. As observed using the third-QSPR approach reported herein, this sigma moments QSPR model is unable to evaluate correctly the lower bubble size in [P$_{66614}$][DCA] than in [C$_{14}$ mim][NTf$_2$] (or [C$_{8}$ mim][NTf$_2$]) while a correct trend is observed in the present case for investigated halide-based ILs. This further validates the possibility to use the sigma moments to setup QSPR applications without prior knowledge of any experimental descriptors.

**Conclusions**

Average bubble size and bubble size distributions have been reported for 11 ILs with various cation ([P$_{66614}$], [C$_2$ mim], [C$_4$ mim] and [C$_{mpyr}$]) and anion (Br$^-$, Cl$^-$, DCA, TFA, ETSO$_4^-$, Dec and NTf$_2$) combinations. Correlation of the bubble size data to the physico-chemical properties of each IL showed only general, qualitative trends with poor correlations. It was, therefore, concluded that no individual physical property was the determining factor. However, it was noted that the strongest correlations were observed with contact angle and viscosity. A QSPR-based model approach was also used to investigate these key properties but was unable to provide a strong correlation or reproduce the experimental trend observed. Therefore, QSPR models were used to relate the strength of the anion and cation interaction (as described by COSMOthermX generated sigma profiles and sigma surfaces) with the bubble size observed and this approach showed an increased degree of correlation. However, the strongest relationship was observed ($R^2 = 0.98$ and RAAD = 13%) when the physicochemical parameters for each IL was neglected and only the sigma moments were used to describe the ILs. This final approach was the most successful at reproducing the experimental trend for all ILs and bubble size ranges investigated. The use of this model to accurately reproduce the experimental results shows the potential for selection or design of an IL with a specific average bubble size and could be very useful in the implementation of such materials in gas capture applications. This study has demonstrated that it is possible to generate microbubbles in ionic liquids which has the potential to lead to increased kinetics for gas separation processes. Importantly, the predictive model which has been developed provides a path for process design based on bubble size as well as the thermodynamics of gas absorption in ionic liquids which has been reported previously.

**Acknowledgements**

This work was carried out as part of the EPSRC funded “4CU” programme grant, aimed at sustainable conversion of carbon dioxide into fuels, led by The University of Sheffield and carried out in collaboration with The University of Manchester, Queen’s University Belfast and University College London (EP/K001329/1). The authors also acknowledge funding from the EPSRC under the grant no. EP/N009533/1.

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Factors Affecting Bubble Size in Ionic Liquids
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Bubble behaviour of 11 ionic liquids was studied and the relationship of bubble size, physical properties and structure was examined.