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Practical Determination of the Solubility Parameters of 1-Alkyl-3-methylimidazolium Bromide ([C<sub>n</sub>C<sub>1</sub>im]Br, n = 5, 6, 7, 8) Ionic Liquids by Inverse Gas Chromatography and the Hansen Solubility Parameter

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Abstract: The physicochemical properties of four 1-alkyl-3-methylimidazolium bromide ([C<sub>n</sub>C<sub>1</sub>im]Br, n = 5, 6, 7, 8) ionic liquids (ILs) were investigated in this work by using inverse gas chromatography (IGC) from 303.15 K to 343.15 K. Twenty-eight organic solvents were used to obtain the physicochemical properties between each IL and solvent via the IGC method, including the specific retention volume and the Flory–Huggins interaction parameter. The Hildebrand solubility parameters of the four [C<sub>n</sub>C<sub>1</sub>im]Br ILs were determined by linear extrapolation to be $\delta_2([C_5C_1im]Br) = 25.78$ (J·cm<sup>-3</sup>)<sup>0.5</sup>, $\delta_2([C_6C_1im]Br) = 25.38$ (J·cm<sup>-3</sup>)<sup>0.5</sup>, $\delta_2([C_7C_1im]Br) = 24.81$ (J·cm<sup>-3</sup>)<sup>0.5</sup> and $\delta_2([C_8C_1im]Br) = 24.33$ (J·cm<sup>-3</sup>)<sup>0.5</sup> at room temperature (298.15 K). At the same time, the Hansen solubility parameters of the four [C<sub>n</sub>C<sub>1</sub>im]Br ILs were simulated by using the Hansen Solubility Parameter in Practice (HSPiP) at room temperature (298.15 K). The results were as follows: $\delta_i([C_5C_1im]Br) = 25.86$ (J·cm<sup>-3</sup>)<sup>0.5</sup>, $\delta_i([C_6C_1im]Br) = 25.39$ (J·cm<sup>-3</sup>)<sup>0.5</sup>, $\delta_i([C_7C_1im]Br) = 24.81$ (J·cm<sup>-3</sup>)<sup>0.5</sup> and $\delta_i([C_8C_1im]Br) = 24.33$ (J·cm<sup>-3</sup>)<sup>0.5</sup>. These values were slightly higher than those obtained by the IGC method, but they only exhibited small errors, covering a range of 0.01 to 0.1 (J·cm<sup>-3</sup>)<sup>0.5</sup>. In addition, the miscibility between the IL and the probe was evaluated by IGC, and it exhibited a basic agreement with the HSPiP. This study confirms that the combination of the two methods can accurately calculate solubility parameters and select solvents.

Keywords: ionic liquids; Hansen solubility parameter in practice; Hildebrand solubility parameter; inverse gas chromatography

1. Introduction

Ionic liquids (ILs), as demonstrated by green and neoteric solvent research in recent years [1,2], are salts that are commonly made up of asymmetric organic cations, and either inorganic or organic anions [3]. ILs have been widely used as novel electrolytes, separation solvents, and reaction media [4,5], due to their excellent thermal stability, adjustable density, low melting point, strong solvation and high electrochemical stability [6,7]. However, their cost and high viscosity hinders their application. Knowledge about the thermophysical properties of each ionic liquid is essential for scaling up its potential applications. Moreover, 1-alkyl-3-methylimidazolium bromides ([C<sub>n</sub>C<sub>1</sub>im]Br) are one of the most commonly investigated types of ILs, solely for their use as an intermediate compound.
Ma [8] separated algae within an entire aquatic ecosystem, according to their stability and high solubility of \([\text{C}_n\text{C}_1\text{im}]\text{Br}\) \((n = 4, 6, 8, 10, 12)\). In addition, he found that the acute toxicities of these ionic liquids were positively correlated with the alkyl chain length of imidazolium-based ILs. This indicated that \([\text{C}_{12}\text{C}_3\text{im}]\text{Br}\)-separated algae was the best, and it could be stored in purified water. Ekka [9] removed Pb(II) from an aqueous solution using \([\text{C}_n\text{C}_1\text{im}]\text{Br}\) \((n = 4, 10, 16)\) as a template-synthesized mesoporous silica, because \([\text{C}_n\text{C}_1\text{im}]\text{Br}\) has a high thermal stability, and it is reusable and amphiphilic. The results showed that the ILs bearing a longer alkyl chain \([\text{C}_{16}\text{C}_1\text{im}]\text{Br}\) were suitable adsorbents for Pb (II) removal, due to their surface area increasing with the increase of carbon chain length. The use of ILs is of great significance in promoting the removal of metals from water.

For a clearer understanding of how the intermolecular interactions of two components influence their applications, many researchers have studied different parameters that are relevant to ILs [10]. The Flory–Huggins interaction parameter \((\chi)\) is a vital tool that is used to predict the thermodynamic state of ILs and select suitable solvents [11]. The Hildebrand solubility parameter \((\delta_2)\) is a physical and chemical parameter that is inherent to a substance, which is commonly used in the formulation design, chemical additive distribution, solvent selection, and system stability studies and membrane penetration [12,13]. The Hildebrand solubility parameter is usually obtained by dynamic mechanical analysis, titration methods, swelling measurements, group contribution calculation methods, and viscosity measurements [14,15]. However, these methods are often time-consuming and laborious. Thus, inverse gas chromatography (IGC) has been applied to the study of the thermodynamic properties of polymers, carbon blacks, ILs, and other materials [16,17]. In addition, Dr. Charles M. Hansen has proposed the Hansen solubility parameter (HSP) theory, which splits the Hildebrand solubility parameter into three parts: the dispersive interactions, \(\delta_D\), the polar interactions, \(\delta_P\), and the hydrogen bonding interactions, \(\delta_H\). Furthermore, he has developed software known as the Hansen Solubility Parameter in Practice (HSPiP) [18], which uses a genetic algorithm to calculate HSPs [19]. Recently, Ni [20] researched the solubility parameters of alkali lignins using IGC and HSPiP, and found that acetone was a moderately suitable solvent for alkali lignins. It has been confirmed that IGC and HSPiP can be used to determine the solubility parameters of materials, and they are useful for solvent selection. Yu [21] determined the solubility parameters of \([\text{C}_n\text{C}_1\text{im}][\text{OAC}]\) \((n = 2, 4, 6, 8)\) by IGC and HSPiP, and found that the results were the same. This provides another method for determining the solubility parameters of ILs. Liu [22] has researched the HSP of hydrogenated nitrile rubber (HNBR) by IGC and HSPiP, and has calculated the energy differences \((R_a)\) between HNBR and solvents or solvent mixtures according to their HSP values. In addition, he found that the swelling volume decreases with increasing \(R_a\) values. Therefore, it may be possible to use HSP to predict the swelling phenomena of cured rubber articles in mixed fluids, such as bio-fuels or lubricants. However, solubility parameter data that are related to \([\text{C}_n\text{C}_1\text{im}]\text{Br}\) \((n = 5, 6, 7, 8)\) have not been reported.

In this study, a widely used method, the IGC method, is proposed for the calculation of the miscibility and \(\delta_2\) of ILs in various solvents. In addition, HSPiP software is used to calculate the miscibilities and HSPs of four ILs via solubility testing, and a comparative study with the results derived from the IGC is performed.

2. Results

2.1. Hildebrand Solubility Parameter

2.1.1. Miscibility of the IL and the Probe

The specific retention volume, \(V^0_g\), at the zero-pressure standard state was determined experimentally from Equation (1) [23,24], which is:

\[
V^0_g = \frac{273.15}{mT_a} F \frac{P_0 - P_w}{P_0} (t_r - t_0)^3 \left( \frac{P_i}{P_0} \right)^2 - 1 - \frac{1}{2} \left( \frac{P_i}{P_0} \right)^3 - 1
\]
where \( t_r \) is the retention time of the probe, \( T_a \) is the room temperature, and \( F \) is the flow rate of carrier gas, \( m \) is the mass of the IL on the column, \( t_0 \) is the retention time of the non-interacting probe, \( P_w \) represents the saturated vapor pressure, and \( P_0 \) and \( P_1 \) are the outlet and inlet pressures of the column, respectively.

The specific retention volume, \( V_g^0 \), is an important term used in determining the thermodynamic parameters of the IL by the IGC. \( V_g^0 \) of 28 probes on four ILs from 303.15 K to 343.15 K were calculated by Equation (1). The results are listed in Table S1. To obtain the retention graph of the probes, \( \ln V_g^0 \) was plotted with the temperatures from 303.15 K to 343.15 K. For \([\text{C}_{5}\text{C}_{1}\text{im}]\text{Br}\), Figure 1 demonstrates that the \( \ln V_g^0 \) value decreased with increasing temperature. In addition, a linear relationship between the probe and \([\text{C}_{5}\text{C}_{1}\text{im}]\text{Br}\) was obtained within the range of the experimental temperature. This results indicated that a balance had been established between the probe and \([\text{C}_{5}\text{C}_{1}\text{im}]\text{Br}\). For the \( n \)-alkane series, the \( V_g^0 \) increased as the numbers of \( \text{CH}_2 \) groups increased because of the increase of the interaction forces between the IL and the probe caused by the greater amount of \( \text{CH}_2 \) added into the probe.

![Figure 1. \([\text{C}_{5}\text{C}_{1}\text{im}]\text{Br}\): Plot of \( \ln V_g^0 \) versus 1000K/T for the probes: (a) \( n \)-C_6, \( n \)-C_7, \( n \)-C_8, \( n \)-C_9, \( n \)-C_10, \( n \)-C_11, \( n \)-C_12; (b) benzene, toluene, \( \alpha \)-xylene, \( \beta \)-xylene, ethyl benzene, \( n \)-propyl benzene, \( n \)-butyl benzene; (c) cyclohexene, octene, pentanone, 3-pentanone, thiophene, nitromethane, \( \beta \)-xylene; (d) methanol, ethanol, propanol, isopropanol, butanol, 2-butanol, isobutanol.](image)

The Flory–Huggins interaction parameter, \( \chi_{12} \), which was obtained using IGC experiments, was calculated by using the expression [13,25].

\[
\chi_{12} = \ln \left( \frac{273.15 R V_2}{P_1^0 V_g^0 V_1} \right) - 1 - \frac{P_1^0 (B_{11} - V_1)}{R T}
\]

where \( V_2 \) is the specific volume of the IL, \( T \) is the column temperature, \( V_1 \) is the molar volume of the probes, \( P_1^0 \) represents the probe vapor pressure at the column temperature, \( R \) represents the...
gas constant, and $B_{11}$ is the second virial coefficient of the probe, where the probe solvent solubility parameter, $\delta_{12}$, can be obtained from the literature acquired by using Equation (3) [26], which is:

$$B_{11}/V_c = 0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n - 1)(T_c/T)^{1.5}$$

where $V_c$ is the critical molar volume of the solvent, $T_c$ represents the critical temperature of the solvent [27], and $n$ is the number of carbon atoms in the solute.

The Flory–Huggins interaction parameter, $\chi_{12}$, plays a significant role in predicting the miscibility between the IL and the probe. The $\chi_{12}$ values were calculated according to Equation (2), as listed in Table 1, which shows that $\chi_{12}$ of some probes, such as thiophene, increased when the temperature increased. However, $\chi_{12}$ of other probes, such as $n$-butyl benzene, $o$-xylene, $m$-xylene, $p$-xylene, ethyl benzene, toluene, nitromethane, methanol, ethanol, $n$-propyl benzene, cyclohexene, octene, pentanone, 3-pentanone, propanol, benzene, isopropanol, butanol, $n$-C$_6$ to $n$-C$_{12}$, 2-butanol, and isobutanol decreased when the temperature increased. The reasons for this change in $\chi_{12}$ may include: enthalpy, $\chi_{12}$, and entropic, $\chi_{S}$ [28]. $\chi_{12}$ is related to the intermolecular forces between the IL and the probe, which gradually decrease with increasing temperature. Compared with the enthalpy, $\chi_{S}$ displays an opposite, trend, and it is associated with the free solvent volume. The decrease in the $\chi_{12}$ value means that the IL–probe interactions are becoming strong. According to the Flory–Huggins theory, an $\chi_{12}$ value below 0.5, indicates that the IL and the probe are completely miscible. By contrast, an $\chi_{12}$ value above 0.5 indicates that the IL and probe are insoluble or partially dissolved. In other words, a low $\chi_{12}$ value reflects good compatibility. The following rules have been developed for the system [29,30]: an $\chi_{12}$ value that is lower than 0.5 indicates that the solvent is good, and a value of between 0.5 and 1 indicates a moderately suitable solvent, whereas a $\chi_{12}$ value that is larger than 1 indicates a poor solvent. The results are listed in Table 1. The $\chi_{12}$ values indicated that nitromethane, methanol, ethanol, butanol, thiophene, 2-butanol, isopropanol, propanol, and isobutanol were excellent solvents for all of the examined ILs. By contrast, $n$-propyl benzene, cyclohexene, ethyl benzene, $o$-xylene, $m$-xylene, $p$-xylene, the $n$-alkanes ($n$-C$_6$ to $n$-C$_{12}$), octane, and $n$-butyl benzene were poor solvents for all of the examined ILs. Table 1 shows that at the same temperature, the best solvents for dissolving the four ILs were alcohols, followed by benzenes and $n$-alkanes. This finding was related to the polarities of the solvents.

**Table 1.** The Flory–Huggins interaction parameter, $\chi_{12}$, between the probe and IL at various temperatures for the hypothetical liquid at zero pressure.

| Probes | ILs          | $\chi_{12}$ |
|--------|--------------|-------------|
| $n$-C$_6$ | [C$_6$C$_1$im]Br | 3.33, 3.22, 3.16, 2.96, 2.91 |
|        | [C$_6$C$_1$im]Br | 3.20, 3.16, 3.13, 2.89, 2.80 |
|        | [C$_7$C$_1$im]Br | 3.00, 2.85, 2.82, 2.79, 2.71 |
|        | [C$_8$C$_1$im]Br | 2.38, 2.35, 2.32, 2.29, 2.19 |
| $n$-C$_7$ | [C$_6$C$_1$im]Br | 3.27, 3.18, 3.13, 3.06, 2.99 |
|        | [C$_7$C$_1$im]Br | 3.19, 3.10, 3.01, 2.97, 2.95 |
|        | [C$_8$C$_1$im]Br | 2.94, 2.81, 2.77, 2.71, 2.65 |
|        | [C$_9$C$_1$im]Br | 2.43, 2.37, 2.33, 2.29, 2.24 |
| $n$-C$_8$ | [C$_6$C$_1$im]Br | 3.26, 3.19, 3.13, 3.09, 3.04 |
|        | [C$_7$C$_1$im]Br | 3.12, 3.01, 2.94, 2.91, 2.88 |
|        | [C$_8$C$_1$im]Br | 2.97, 2.73, 2.69, 2.67, 2.65 |
|        | [C$_9$C$_1$im]Br | 2.42, 2.39, 2.35, 2.31, 2.28 |
| $n$-C$_9$ | [C$_6$C$_1$im]Br | 3.39, 3.30, 3.22, 3.16, 3.10 |
|        | [C$_7$C$_1$im]Br | 3.17, 3.06, 2.97, 2.91, 2.83 |
|        | [C$_8$C$_1$im]Br | 3.02, 2.93, 2.84, 2.77, 2.70 |
|        | [C$_9$C$_1$im]Br | 2.61, 2.54, 2.47, 2.40, 2.33 |
| Probes      | ILs                  | $\chi_{12}$ |
|-------------|----------------------|-------------|
|             |                      | 303.15 K    | 313.15 K    | 323.15 K    | 333.15 K    | 343.15 K    |
| n-C_{10}    | [C_{6}C_{1}im]Br     | 3.47        | 3.38        | 3.28        | 3.20        | 3.13        |
|             | [C_{6}C_{1}im]Br     | 3.36        | 3.14        | 3.05        | 2.98        | 2.89        |
|             | [C_{6}C_{1}im]Br     | 3.13        | 3.02        | 2.94        | 2.86        | 2.79        |
|             | [C_{6}C_{1}im]Br     | 2.70        | 2.62        | 2.54        | 2.46        | 2.39        |
| n-C_{11}    | [C_{6}C_{1}im]Br     | 3.62        | 3.51        | 3.41        | 3.33        | 3.23        |
|             | [C_{6}C_{1}im]Br     | 3.43        | 3.31        | 3.22        | 3.12        | 3.02        |
|             | [C_{6}C_{1}im]Br     | 3.31        | 3.18        | 3.09        | 3.00        | 2.91        |
|             | [C_{6}C_{1}im]Br     | 2.85        | 2.76        | 2.66        | 2.58        | 2.50        |
| n-C_{12}    | [C_{6}C_{1}im]Br     | 3.76        | 3.63        | 3.55        | 3.44        | 3.34        |
|             | [C_{6}C_{1}im]Br     | 3.58        | 3.47        | 3.36        | 3.27        | 3.17        |
|             | [C_{6}C_{1}im]Br     | 3.49        | 3.36        | 3.26        | 3.13        | 3.06        |
| benzene     | [C_{6}C_{1}im]Br     | 3.04        | 2.92        | 2.81        | 2.70        | 2.65        |
|             | [C_{6}C_{1}im]Br     | 0.580       | 0.551       | 0.503       | 0.465       | 0.414       |
|             | [C_{6}C_{1}im]Br     | 0.646       | 0.603       | 0.582       | 0.539       | 0.486       |
|             | [C_{6}C_{1}im]Br     | 0.695       | 0.660       | 0.630       | 0.607       | 0.538       |
| toluene     | [C_{6}C_{1}im]Br     | 0.781       | 0.758       | 0.733       | 0.696       | 0.640       |
|             | [C_{6}C_{1}im]Br     | 0.892       | 0.850       | 0.822       | 0.742       | 0.699       |
| o-xylene    | [C_{6}C_{1}im]Br     | 0.973       | 0.920       | 0.882       | 0.783       | 0.758       |
|             | [C_{6}C_{1}im]Br     | 1.04        | 0.980       | 0.844       | 0.826       | 0.808       |
| m-xylene    | [C_{6}C_{1}im]Br     | 1.00        | 0.962       | 0.947       | 0.918       | 0.893       |
|             | [C_{6}C_{1}im]Br     | 1.08        | 1.03        | 1.01        | 0.823       | 0.804       |
|             | [C_{6}C_{1}im]Br     | 1.14        | 1.07        | 1.05        | 0.909       | 0.865       |
|             | [C_{6}C_{1}im]Br     | 1.15        | 1.10        | 0.961       | 0.933       | 0.918       |
|             | [C_{6}C_{1}im]Br     | 1.10        | 1.06        | 1.03        | 1.00        | 0.970       |
| p-xylene    | [C_{6}C_{1}im]Br     | 1.09        | 1.07        | 1.06        | 1.04        | 1.02        |
|             | [C_{6}C_{1}im]Br     | 1.16        | 1.11        | 1.09        | 1.07        | 1.07        |
|             | [C_{6}C_{1}im]Br     | 1.26        | 1.21        | 1.18        | 1.15        | 1.11        |
| ethyl benzene| [C_{6}C_{1}im]Br     | 1.11        | 1.08        | 1.07        | 1.06        | 1.04        |
|             | [C_{6}C_{1}im]Br     | 1.23        | 1.18        | 1.16        | 1.12        | 1.09        |
| n-propyl benzene| [C_{6}C_{1}im]Br | 1.23        | 1.20        | 1.13        | 0.957       | 0.933       |
|             | [C_{6}C_{1}im]Br     | 1.26        | 1.20        | 1.15        | 1.04        | 1.00        |
|             | [C_{6}C_{1}im]Br     | 1.13        | 1.05        | 1.04        | 1.03        | 1.00        |
|             | [C_{6}C_{1}im]Br     | 1.23        | 1.16        | 1.13        | 1.10        | 1.06        |
| n-butyl benzene| [C_{6}C_{1}im]Br   | 1.56        | 1.48        | 1.44        | 1.25        | 1.21        |
|             | [C_{6}C_{1}im]Br     | 1.26        | 1.22        | 1.18        | 1.16        | 1.11        |
|             | [C_{6}C_{1}im]Br     | 1.34        | 1.29        | 1.24        | 1.20        | 1.17        |
|             | [C_{6}C_{1}im]Br     | 1.35        | 1.30        | 1.26        | 1.22        | 1.18        |
| cyclohexene | [C_{6}C_{1}im]Br     | 1.82        | 1.75        | 1.69        | 1.47        | 1.42        |
|             | [C_{6}C_{1}im]Br     | 1.46        | 1.40        | 1.37        | 1.33        | 1.28        |
| octene      | [C_{6}C_{1}im]Br     | 2.28        | 2.08        | 2.05        | 2.02        | 1.92        |
|             | [C_{6}C_{1}im]Br     | 2.09        | 2.01        | 1.96        | 1.91        | 1.87        |
|             | [C_{6}C_{1}im]Br     | 2.15        | 2.02        | 1.98        | 1.92        | 1.90        |
|             | [C_{6}C_{1}im]Br     | 2.13        | 2.02        | 1.97        | 1.92        | 1.90        |
|             | [C_{6}C_{1}im]Br     | 2.86        | 2.78        | 2.73        | 2.68        | 2.63        |
|             | [C_{6}C_{1}im]Br     | 2.71        | 2.59        | 2.57        | 2.50        | 2.47        |
|             | [C_{6}C_{1}im]Br     | 2.51        | 2.43        | 2.40        | 2.36        | 2.31        |
2.1.2. The Hildebrand Solubility Parameter

The Hildebrand solubility parameter is defined as the square root of the cohesive energy (CED) \([31]\).

\[
\delta_1 = \left( \frac{\Delta E_v}{V_1} \right)^{1/2} = \left( \frac{\Delta H_v - RT}{V_1} \right)^{1/2} = \left( CED \right)^{1/2}
\]

where \(\Delta E_v\) is the energy of vaporization, \(V_1\) is the molar volume, and \(\Delta H_v\) is molar enthalpy of evaporation.
For the ILs, the calculation formula for the Hildebrand solubility parameter, $\delta_2$, was calculated using the following equation [32,33]:

$$
\left( \frac{\delta_1^2}{RT} - \frac{\chi_{12}}{V_1} \right) = \left( \frac{2\delta_2}{RT} \right)\delta_1 - \frac{\delta_2}{RT} 
$$

(5)

By plotting the left-hand side of Equation (5) as a function of the probe solubility parameter $\delta_1$ at different temperatures [34], $\delta_2$ was obtained from the slope of the straight line.

The variable $\delta_2$ plays a significant role in selecting solvents to dissolve or swell materials, judging the compatibility of blends, and selecting the pharmaceutical solvents. The $\delta_2$ for the IL [C<sub>5</sub>C<sub>1</sub>im]Br from 303.15 K to 343.15 K was calculated from $\frac{\delta_1^2}{RT} - \frac{\chi_{12}}{V_1}$ versus $\delta_1$, as shown in Figure 2. The $\frac{\delta_1^2}{RT} - \frac{\chi_{12}}{V_1}$ versus $\delta_1$ graphs for the three ILs are shown in Figures S1–S3. The $\delta_2$ of the four examined ILs and the literature are given in Table 2. As shown in Table 2, the increase of temperature from 303.15 to 343.15 K is accompanied by a decrease in the $\delta_2$ of the four ILs, varying within the ranges of 25.71–25.21 (J·cm<sup>-3</sup>)<sup>0.5</sup>, 25.32–24.82 (J·cm<sup>-3</sup>)<sup>0.5</sup>, 24.70–24.22 (J·cm<sup>-3</sup>)<sup>0.5</sup>, and 24.11–23.58 (J·cm<sup>-3</sup>)<sup>0.5</sup>, respectively. The $\delta_2$ shows a slight decrease with increasing temperature, something that has also been observed by Marciniak [35] and Moganty [36]. As the temperature increases, the $\delta_2$ values decrease, because the molar enthalpy of evaporation decreases with temperature, and the molar volume increases with temperature. We also found that $\delta_2$ decreases with increasing alkyl chain length at same temperature, due to the molar enthalpy of evaporation decreasing with the molar mass increase of cations, which is in agreement with the results reported by Alavianmehr [37] and Marciniak [38]. In other words, the more aliphatic the character of the imidazolium cation, the lower the solubility parameters. In addition, we were able to obtain the $\delta_2$ of the ILs at room temperature, using the extrapolation method, based on the relationship curve seen in Figure 3. The $\delta_2$ values of three ILs at 298.15 K are shown in Table 2. They also follow the rule: [C<sub>5</sub>C<sub>1</sub>im]Br > [C<sub>6</sub>C<sub>1</sub>im]Br > [C<sub>7</sub>C<sub>1</sub>im]Br > [C<sub>8</sub>C<sub>1</sub>im]Br.
Three ILs at 298.15 K are shown in Table 2. They also follow the rule: 

\[ [\text{C}_5\text{C}_1\text{im}]\text{Br} > [\text{C}_6\text{C}_1\text{im}]\text{Br} > [\text{C}_7\text{C}_1\text{im}]\text{Br} \]

Figure 2. Variation of the term \( \frac{\delta_1^2}{RT} - \frac{\chi_{12}}{V_1} \) with solubility parameters of the solvent \( \delta_1 \) in 

\([\text{C}_5\text{C}_1\text{im}]\text{Br}\) (a) at 303.15 K; (b) at 313.15 K; (c) at 323.15 K; (d) at 333.15 K; (e) at 343.15 K.
Table 2. The Hildebrand solubility parameter, $\delta_2$, of ILs at various temperatures taken from the literature for the hypothetical liquids at zero pressure.

| ILs                  | T/(K) | $\delta_2$/(J·cm$^{-3}$)$^{0.5}$ | Reference |
|----------------------|-------|----------------------------------|-----------|
| [C$_4$C$_1$pip][SCN] | 298.15| 30.70                            | [35]      |
|                     | 318.15| 30.10                            |           |
|                     | 328.15| 29.80                            |           |
|                     | 338.15| 29.50                            |           |
|                     | 348.15| 29.10                            |           |
|                     | 358.15| 28.80                            |           |
| [C$_2$C$_1$im][TfO] | 283.15| 23.10                            | [36]      |
|                     | 298.15| 23.00                            |           |
|                     | 313.15| 22.90                            |           |
| [C$_4$C$_1$im][PF$_6$] | 298.15| 29.80                            | [37]      |
| [C$_6$C$_1$im][PF$_6$] | 298.15| 28.60                            |           |
| [C$_8$C$_1$im][PF$_6$] | 298.15| 27.80                            |           |
| [C$_2$C$_1$im][BF$_4$] | 298.15| 24.40                            | [38]      |
| [C$_4$C$_1$im][BF$_4$] | 298.15| 24.30                            |           |
| [C$_6$C$_1$im][BF$_4$] | 298.15| 23.30                            |           |
| [C$_4$C$_1$im][NTf$_2$] | 298.15| 26.70                            |           |
| [C$_6$C$_1$im][NTf$_2$] | 298.15| 25.60                            |           |
| [C$_8$C$_1$im][NTf$_2$] | 298.15| 25.00                            |           |
| [C$_4$C$_1$im][SCN]  | 298.15| 24.64                            |           |
| [C$_6$C$_1$im][SCN]  | 298.15| 23.65                            |           |
| [C$_5$C$_1$im]Br     | 298.15| 25.78 $^a$                       | In this work |
| [C$_6$C$_1$im]Br     | 303.15| 25.78 $^a$                       | In this work |
| [C$_5$C$_1$im]Br     | 303.15| 25.71                            |           |
| [C$_6$C$_1$im]Br     | 313.15| 25.59                            |           |
| [C$_5$C$_1$im]Br     | 323.15| 25.48                            |           |
| [C$_6$C$_1$im]Br     | 333.15| 25.32                            |           |
| [C$_5$C$_1$im]Br     | 343.15| 25.21                            |           |
| [C$_7$C$_1$im]Br     | 298.15| 25.38 $^a$                       | In this work |
| [C$_8$C$_1$im]Br     | 303.15| 24.78 $^a$                       | In this work |
| [C$_7$C$_1$im]Br     | 303.15| 24.70                            |           |
| [C$_8$C$_1$im]Br     | 313.15| 24.51                            |           |
| [C$_7$C$_1$im]Br     | 323.15| 24.35                            |           |
| [C$_8$C$_1$im]Br     | 333.15| 24.18                            |           |
| [C$_7$C$_1$im]Br     | 343.15| 24.02                            |           |
| [C$_8$C$_1$im]Br     | 298.15| 24.23 $^a$                       | In this work |
| [C$_8$C$_1$im]Br     | 303.15| 24.11                            |           |
| [C$_8$C$_1$im]Br     | 313.15| 24.06                            |           |
| [C$_8$C$_1$im]Br     | 323.15| 23.94                            |           |
| [C$_8$C$_1$im]Br     | 333.15| 23.75                            |           |
| [C$_8$C$_1$im]Br     | 343.15| 23.58                            |           |

Standard uncertainties are as follows: $u$(T) = ±0.5 K, $u$(δ$_2$) = 0.02 (J·cm$^{-3}$)$^{0.5}$. $^a$: Obtained by extrapolation.
We found that good and poor solvents could be obtained from the RED values. The four ILs

\[ \delta = a + b \delta \]

where \(\delta\) is the solubility parameter, namely, polar (\(\delta_p\), hydrogen bonding (\(\delta_H\)) and dispersion (\(\delta_D\)) [39–41]:

\[
\delta^2_i = \delta_D^2 + \delta_H^2 + \delta_p^2
\]

(6)

2.2. Hansen Solubility Parameter

According to the HSP concept, the total solubility parameter (\(\delta_i\)) of an IL can be divided into partial solubility parameters, namely, polar (\(\delta_p\)), hydrogen bonding (\(\delta_H\)) and dispersion (\(\delta_D\)) [39–41]:

\[
\delta^2_i = \delta_D^2 + \delta_H^2 + \delta_p^2
\]

(6)

The distance (\(R_a\)) between the solvent and the IL within a three-dimensional (3D) diagram was calculated using Equation (7) [42,43]:

\[
R_a = [4(\delta_D^2 - \delta_D^2) + (\delta_H^2 - \delta_H^2) + (\delta_H^2 - \delta_H^2)]^{1/2}
\]

(7)

The relative energy difference (RED), which plays a significant role in predicting the compatibility of the IL and the solvent, can be calculated by Equation (8):

\[
RED = \frac{R_a}{R_0}
\]

(8)

where \(R_0\) is the interaction radius of the IL, \(R_a\) is the distance between the solvent and center of the solubility sphere, \(\delta_D^2\) represents the HSP for the IL, and \(\delta_D^2\) is the HSP for the solvent. RED ≤ 1 indicates a good solvent, while a progressively higher RED value implies a poor solvent.

The double-sphere is divided into two domains (the blue solid blue ball at the center represents \(D_1\), and the green ball represents \(D_2\)). The Hansen solubility parameters of the ILs can be acquired by Equation (9)–(11) [44], which are:

\[
a = \frac{R_{01}}{R_{01} + R_{02}}
\]

(9)

\[
b = \frac{R_{02}}{R_{01} + R_{02}}
\]

(10)

\[
\delta_i(\text{Midpoint}) = a \times \delta_1 + b \times \delta_2
\]

(11)

where \(\delta_1\) and \(\delta_2\) are the solubility parameters of the \(D_1\) and \(D_2\) domains, \(R_{01}\) are the interaction radii of the \(D_1\) domain, \(R_{02}\) represent the interaction radii of the \(D_2\) domain, and \(\delta_i\) (the Midpoint) is a solubility parameter that considers the volume of spheres.

2.2.1. Solubility Test for ILs

The solubility test results of each ionic liquid in 51 pure solvents are summarized in Table 3. We found that good and poor solvents could be obtained from the RED values. The four ILs were found to be poorly dissolved in \(n\)-propyl benzene, \(m\)-xylene, cyclohexene, \(o\)-xylene, ethyl benzene, \(p\)-xylene, \(n\)-C_6, \(n\)-C_7, \(n\)-C_8, \(n\)-C_9, \(n\)-C_10, \(n\)-C_11, \(n\)-C_12, octane, and \(n\)-butyl benzene, whereas
nitromethane, methanol, ethanol, butanol, thiophene, 2-butanol, isopropanol, propanol, and isobutanol were favorable solvents for the four examined ILs. These results are basically consistent with those derived from IGC, based on the $\chi_{12}$ values. The determination of the miscibility between the IL and the probe by HSPiP is a supplement to the determination of IGC, due to the huge amount of HSPiP data. In practical applications, the combination of the two methods can accurately select solvents.

| Table 3. Solubility test results. |
|-----------------------------------|
| Solvents         | HSP/$\text{j cm}^{-3}\cdot\text{mol}^{-1}$ | $[\text{C}_5\text{C}_1\text{im}]\text{Br}$ | $[\text{C}_6\text{C}_1\text{im}]\text{Br}$ | $[\text{C}_7\text{C}_1\text{im}]\text{Br}$ | $[\text{C}_8\text{C}_1\text{im}]\text{Br}$ |
|------------------|---------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|
| acetonitrile     | 15.3 18.0 6.1 1 0.995 1 0.886 1 0.857 1 1.165 | $\sigma$                                  | $\delta$                                  | $\rho$                                  | $\tau$                                  |
| 2-butanol        | 15.8 5.7 14.5 1 0.925 1 0.934 1 0.768 1 0.642 | $\sigma$                                  | $\delta$                                  | $\rho$                                  | $\tau$                                  |
| butanol          | 16.0 5.7 15.8 1 0.800 1 0.777 1 0.632 1 0.591 | $\sigma$                                  | $\delta$                                  | $\rho$                                  | $\tau$                                  |
| tetrahydrofuran  | 16.8 5.7 8.0 1 1.043 $\ast$ 1 0.902 1 0.935 1 0.977 | $\sigma$                                  | $\delta$                                  | $\rho$                                  | $\tau$                                  |
| isobutanol       | 15.1 5.7 15.9 1 0.882 1 0.884 1 0.680 1 0.516 | $\sigma$                                  | $\delta$                                  | $\rho$                                  | $\tau$                                  |
| ethylene glycol   | 17.0 11.0 26.0 1 0.944 1 0.753 1 0.605 1 0.914 | $\sigma$                                  | $\delta$                                  | $\rho$                                  | $\tau$                                  |
| isopropanol      | 15.8 6.9 16.4 1 0.724 1 0.692 1 0.546 1 0.501 | $\sigma$                                  | $\delta$                                  | $\rho$                                  | $\tau$                                  |
| dichloromethane   | 17.0 7.3 7.1 1 0.906 1 0.781 1 0.847 1 0.848 | $\sigma$                                  | $\delta$                                  | $\rho$                                  | $\tau$                                  |
| ethanol          | 15.8 8.9 19.4 1 0.317 1 0.326 1 0.201 1 0.387 | $\sigma$                                  | $\delta$                                  | $\rho$                                  | $\tau$                                  |
| pyridine         | 19.0 8.8 5.9 1 0.799 1 0.751 1 0.856 1 0.756 | $\sigma$                                  | $\delta$                                  | $\rho$                                  | $\tau$                                  |

$\ast$: Worry out, which means that the Hansen Solubility Parameter in Practice (HSPiP) software prediction should be in the sphere, contrary to the experimental result. $\ast\ast$: Worry in, which means that the HSPiP software prediction should be out of the sphere, contrary to the experimental result.

2.2.2. HSPs of the ILs

Considering $[\text{C}_5\text{C}_1\text{im}]\text{Br}$ as an example, 51 solvents were used to dissolve this. The results of the 3D solubility parameter spheres and the two-dimensional (2D) graphs of the Hansen space are
shown in Figure 4. From Figure 4a, we can see that the green sphere is [C₅C₁im]Br, the blue solid blue ball at the center represents the D₁ domain, and the green ball represents D₂. The blue ball points represent good solvents, and the red data points without the sphere represent solvents, which will, advantageously, not dissolve the IL. Moreover, we can clearly see the solvent distribution from the 2D graphs (Figure 4b). The graphs of HSPs for the other ILs are listed in Figures S4–S6. The simulation results of the four ILs are given in Table 4. The δ₁ values of the four ILs fitted the following rule: [C₅C₁im]Br > [C₆C₁im]Br > [C₇C₁im]Br > [C₈C₁im]Br. The δ₂ values of the ILs decreased with an increase of the alkyl chain. It should be added that the values δ₂ of the four ILs obtained by the HSPiP method were higher than those obtained by IGC. However, the results obtained by both methods were within an error range of 0.01–0.1 (J·cm⁻³)⁰·₅. The harmony between the calculated and experimental values of the solubility parameters is remarkable. The IGC method calculates the δ₂ values through a series of formulas, producing theoretical values, while the HSPiP method is based on solubility testing used to obtain the HSPs of ILs, producing experimental values, which are closer to the true values.

![Figure 4](image-url)

**Figure 4.** (a) The 3D graph with coordinates of [C₅C₁im]Br; (b) The 2D graphs corresponding to the 3D ones of [C₅C₁im]Br.

| ILs      | Domain | δ₁(D) | δ₁(P) | δ₁(H) | δ₁ | δ₂ | R₀  | Fits |
|----------|--------|-------|-------|-------|----|----|-----|------|
| [C₅C₁im]Br | D₁     | 16.89 | 10.28 | 18.87 | 27.33 | -  | 7.1 | 0.974 |
|          | D₂     | 18.40 | 13.85 | 10.58 | 25.34 | -  | 8.7 | 0.974 |
|          | Midpoint | 17.72 | 12.25 | 14.31 | 25.86  | 25.78b | -  |      |
| [C₆C₁im]Br | D₁     | 17.00 | 8.80  | 20.30 | 27.91 | -  | 7.4 |      |
|          | D₂     | 17.90 | 13.20 | 9.50  | 24.18 | -  | 7.9 | 0.962 |
|          | Midpoint | 17.46 | 11.07 | 14.72 | 25.39  | 25.38b | -  |      |
| [C₇C₁im]Br | D₁     | 17.50 | 7.20  | 18.60 | 26.55 | -  | 10.4|      |
|          | D₂     | 17.50 | 14.30 | 8.60  | 24.16 | -  | 7.9 | 0.957 |
|          | Midpoint | 17.50 | 10.27 | 14.28 | 24.81  | 24.75b | -  |      |
| [C₈C₁im]Br | D₁     | 14.94 | 9.37  | 17.12 | 24.58 | -  | 7.5 |      |
|          | D₂     | 18.43 | 12.48 | 10.75 | 24.72 | -  | 8.2 | 0.943 |
|          | Midpoint | 16.76 | 10.99 | 13.79 | 24.33  | 24.23b | -  |      |

*δ₁: Obtained by simulation from the double-sphere type. b: Obtained by extrapolation from the IGC data. Standard uncertainties are as follows: u (δ₁) = 0.03.*
3. Materials and Methods

3.1. Materials

The 1-pentyl-3-methylimidazolium bromide ([C₅C₄im]Br), 1-hexyl-3-methylimidazolium bromide ([C₆C₅im]Br), 1-heptyl-3-methylimidazolium bromide ([C₇C₆im]Br), and 1-octyl-3-methylimidazolium bromide ([C₈C₇im]Br) were supplied by Chengjie Chemical Co., Ltd. (Shanghai, China). The water content and volatile compounds in the ILs were reduced by vacuum evaporation before the experiment. The vacuum evaporation pressure was 0.8 KPa, and the temperature was 363 K. The water content after vacuum evaporation was determined by using the Karl–Fisher titration technique [45], and the mass fraction of the water was less than 600 ppm. The required solvents for the experiment were purchased from J & K Scientific Ltd. (JULABO TitroLine 7750, Germany). All of the studied solvents were used without further purification. The solutes (J & K Scientific Ltd.) with purities better than 0.97 were used without further purification. The CASRN, initial mole fraction purity, initial mole fraction purity, source, and chemical name of the ILs are given in Table S2 in the Supplementary Materials.

3.2. Inverse Gas Chromatography

All experiments were performed on an Agilent 6890 gas chromatograph (Santa Clara, CA, USA) equipped with a flame ionization detector. The detector temperature was kept at 503.15 K and the injector was operated at 523.15 K during all of the experiments. Methane was used to determine the column holdup time, to calculate the retention times of the various probe solvents. High-purity nitrogen was used as a carrier gas, and the flow rate was 20 mL/min. The oven temperature was varied in 10 K intervals, between 303.15 and 343.15 K. Each experiment was repeated at least three times to check its reproducibility.

The stationary phase used in the experiments was prepared by dissolving a weighed sample of the IL in dichloromethane, and then adding it into a weighed amount of 102 silicon alklylation monomer support (80–100 mesh). The mixture was allowed to dry under a rotary evaporator by slow evaporation, to ensure a homogeneous mixture. The chromatographic column was a stainless steel column, with an inner diameter of 2 mm and a length of 1.2 m, and it was purchased from Dalian Ripley Technological Instruments Co., Ltd. (Dalian, China). The coated support was packed into the stainless steel column, and the stationary phase consisted of 20% IL, which was finally heated for 8 h under nitrogen conditions.

3.3. HSPiP Method

To determine the HSP of each IL, its interactions with 51 organic solutes were used to plot the Hansen spheres. A total of 0.2 g IL was placed in a test tube containing 2 mL test solvent. After thorough stirring, the solution was allowed to stand for 24 h at 298.15 K, and dissolution was visually observed. The solvents which could be categorized as good, i.e., those which were totally dissolved in the IL, were given a score of “1”, and poor solvents, which were partially dissolved or insoluble, were given a score of “0”. The experimental data were inputted via HSPiP (Ver.4.1.07, Louisville, KY, USA) to obtain the Hildebrand solubility parameters and HSPs of the ILs.

4. Conclusions

It is necessary to know the solubility parameters of ILs. In this study, the δ₂ values of four ILs were calculated by IGC, and the HSPs of the ILs were determined using the HSPiP method, based on solubility testing. It was found that δ₂ decreased with increasing alkyl chain length, as well as when the temperature increased. At room temperature, the δ₂ values of the four [CₙCₙim]Br ILs considered were consistent across both methods. In addition, the miscibility between the IL and the probe was successfully determined, using X₁₂ values and solubility testing, the results were basically consistent across both methods.
Supplementary Materials: The following are available online, Figure S1: Variation of the term $\delta^2 / RT - \chi_{12} / V_1$ with the solubility parameters of the solvent $\delta_1$ in [C$_6$C$_1$im]Br (a) at 303.15 K; (b) at 313.15 K; (c) at 323.15 K; (d) at 333.15 K; (e) at 343.15 K, Figure S2: Variation of the term $\delta^2 / RT - \chi_{12} / V_1$ with the solubility parameters of the solvent $\delta_1$ in [C$_6$C$_1$im]Br (a) at 303.15 K; (b) at 313.15 K; (c) at 323.15 K; (d) at 333.15 K; (e) at 343.15 K, Figure S3: Variation of the term $\delta^2 / RT - \chi_{12} / V_1$ with the solubility parameters of the solvent $\delta_1$ in [C$_6$C$_1$im]Br (a) at 303.15 K; (b) at 313.15 K; (c) at 323.15 K; (d) at 333.15 K; (e) at 343.15 K, Figure S4: (a) The 3D graph with the coordinates of [C$_6$C$_1$im]Br; (b) The 2D graphs corresponding to the 3D graph of [C$_6$C$_1$im]Br, Figure S5: (a) The 3D graph with the coordinates of [C$_6$C$_1$im]Br; (b) The 2D graphs corresponding to the 3D graph of [C$_6$C$_1$im]Br, Figure S6: (a) The 3D graph with the coordinates of [C$_6$C$_1$im]Br; (b) The 2D graphs corresponding to the 3D graph of [C$_6$C$_1$im]Br, Table S1: The specific retention volume, $V_0^p$, between the probe and IL at various temperatures for the hypothetical liquids at zero pressure, Table S2: Probe description table.

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**Sample Availability:** Samples of the compounds are not available from the authors.