A New Compartmentalized Scale \((P_N)\) for Measuring Polarity 
Applied to Novel Ether-Functionalized Amino Acid Ionic Liquids

Xu Zheng, Chun Guo, Wenqing Wu and Jing Tong *

Abstract: Functionalized and environmentally friendly ionic liquids are required in many fields, but convenient methods for measuring their polarity are lacking. Two novel ether-functionalized amino acid ionic liquids, 1-(2-methoxyethyl)-3-methylimidazolium alanine \([\text{C}_1\text{OC}_2\text{mim}][\text{Ala}]\) and 1-(2-ethoxyethyl)-3-methylimidazolium alanine \([\text{C}_2\text{OC}_2\text{mim}][\text{Ala}]\), were synthesized by a neutralization method and their structures confirmed by NMR spectroscopy. Density, surface tension, and refractive index were determined using the standard addition method. The strength of intermolecular interactions within these ionic liquids was examined in terms of standard entropy, lattice energy, and association enthalpy. A new polarity scale, \(P_N\), is now proposed, which divides polarity into two compartments: the surface and the body of the liquid. Surface tension is predicted via an improved Lorentz-Lorenz equation, and molar surface entropy is used to determine the polarity of the surface. This new \(P_N\) scale is based on easily measured physicochemical parameters, is validated against alternative polarity scales, and is applicable to both ionic and molecular liquids.

Keywords: polarity scale; ionic liquids; ether-functionalized; intermolecular interactions; molar surface entropy; Lorentz-Lorenz equation

1. Introduction

The green chemistry concept is a widely accepted focus of modern chemical research, including the design of new materials. Ionic liquids (ILs) have emerged as useful green reaction media due to their many unique features, such as low vapor pressure and high thermal stability [1,2]. They play important roles in many fields, including energy storage [3], catalysis [4], pharmaceuticals, and medicine [5,6]. However, the relatively high viscosity of ILs is a barrier to further practical applications. Inserting ether groups into the cations of ILs has been shown to substantially reduce their viscosity without lowering thermal stability, while also reducing their toxicity [7–10]. Ether-functionalized ILs (EFILs) have demonstrated remarkable performance in many fields. For example, they dissolve lignocellulosic biomasses [7], reduce viscosity and provide coordination sites for lithium ions in Li/Li-ion batteries [8], and enhance CO\(_2\) selectivity during CO\(_2\) capture [11]. Ether-functionalized ILs (EFILs) have demonstrated remarkable performance in many fields. For example, they dissolve lignocellulosic biomasses [7], reduce viscosity and provide coordination sites for lithium ions in Li/Li-ion batteries [8], and enhance CO\(_2\) selectivity during CO\(_2\) capture [11]. However, traditional ILs containing anions such as Cl\(^-\), BF\(_4\)^-, and PF\(_6\)^- are environmentally hazardous. The development of environmentally friendly, task-specific ILs based on renewable bioresources (such as amino acids and fatty acids) is an environmental necessity. Ohno and Fukumoto were the first to prepare amino acid ILs (AAILs), using 20 different amino acids as the anion; these AAILs demonstrated lower toxicity [12,13]. AAILs have now been utilized in enantioselective separation [14], extraction separation [15], and CO\(_2\) capture [11]. ILs with imidazolium-based cations exhibit low toxicity. Meanwhile, the shorter the alkyl chain on the imidazole ring, the lower the toxicity [16,17]. Thus, imidazolium ILs have proved more attractive than ILs based on ammonium, phosphonium, and pyridinium cations. The
present study describes the preparation of two novel ether-functionalized, imidazolium-based AAILs: 1-(2-methoxyethyl)-3-methylimidazolium alanine (\([\text{C}_1\text{OC}_2\text{mim}][\text{Ala}])\) and 1-(2-ethoxyethyl)-face Tension, and Refractive Index ([\(\text{C}_2\text{OC}_2\text{mim}][\text{Ala}]), together abbreviated as \([\text{C}_n\text{OC}_2\text{mim}][\text{Ala}](n = 1, 2)\).

There is scope for considerable further research into EFILs because their physiochemical properties are highly susceptible to changes in structure. More experimental data are required to elucidate their structure–property relationships. This study measures the density, surface tension, and refractive index of \([\text{C}_n\text{OC}_2\text{mim}][\text{Ala}](n = 1, 2)\). Density correlates with packing efficiency and intermolecular interactions and is a critical design property in chemical engineering [18]. Its study provides insight into the microstructure and macroscopic properties of ILs [19]. Surface tension is a crucial property at liquid–gas interfaces [20], affecting how the phases interact [21]. The surface tension of ILs is between those of alkanes and water [22]. It can be measured directly or predicted using, for example, the parachor formula [23] or group contribution methods [24]. This study predicts surface tension using an improved Lorentz-Lorenz equation. ILs are often used as solvents, so determining their polarity is crucial. Due to their non-structured nature, polarity cannot be determined by traditional methods such as relative permittivity (\(\varepsilon_r\)) and dipole moment (\(\delta\)) [25]. The most widely used experimental method for IL polarity is the \(E_T(30)\) scale, which measures the solvatochromic UV–Vis absorbance shift of a solute. However, this method is time-consuming and expensive, so attempts have been made to develop predictive models [26,27].

The present study proposes a new polarity scale, \(P_N\), which enables polarity to be predicted from the easily measured physicochemical properties of density, surface tension, and refractive index. Following on from our previous studies [28–30], (i) \([\text{C}_n\text{OC}_2\text{mim}][\text{Ala}](n = 1, 2)\) are synthesized and their structures confirmed by nuclear magnetic resonance spectroscopy (NMR); (ii) their density, surface tension, and refractive index are measured from 288.15 to 328.15 K at 5 K intervals; (iii) the strength of their molecular interactions are studied based on standard entropy, lattice energy, and association enthalpy; (iv) an improved Lorentz-Lorenz equation is used to predict the surface tension of ILs and molecular liquids; and (v) a new scale, \(P_N\), for estimating polarity is proposed, combining molar surface entropy \(s\) (which measures the polarity of the surface of a liquid) and the polarity coefficient \(P^2\) (which measures the polarity of the body of a liquid).

2. Results and Discussion

2.1. Density, Surface Tension, and Refractive Index of \([\text{C}_n\text{OC}_2\text{mim}][\text{Ala}](n = 1, 2)\)

The density (\(\rho\)), surface tension (\(\gamma\)), and refractive index (\(n_D\)) of \([\text{C}_n\text{OC}_2\text{mim}][\text{Ala}](n = 1, 2)\) with various water contents over 288.15–328.15 K (at 5 K intervals) are shown in Tables S1–S3 Supplementary Materials, with each value being an average of three measurements using the standard addition method. These parameters were plotted against water content (Figure 1), producing a series of straight lines with correlation coefficient squares (\(r^2\)) consistently greater than 0.99. The y-axis intercepts of these lines give the experimental value of each parameter in anhydrous \([\text{C}_n\text{OC}_2\text{mim}][\text{Ala}](n = 1, 2)\) (Table 1).
Table 1. Density (ρ), surface tension (γ), refractive index (nD), and thermal expansion coefficient (α) at various temperatures (T) for [C_2OC_2mim][Ala] (n = 1, 2).

| T (K) | ρ (g cm⁻³) | γ (mJ m⁻²) | nD | α (K⁻¹ × 10⁴) |
|-------|------------|------------|----|--------------|
| 288.15 | 1.16073    | 51.6       | 1.5112 | 5.8555       |
| 293.15 | 1.15744    | 51.2       | 1.5097 | 5.8722       |
| 298.15 | 1.15423    | 50.9       | 1.5080 | 5.8885       |
| 303.15 | 1.15082    | 50.5       | 1.5066 | 5.9060       |
| 308.15 | 1.14739    | 50.0       | 1.5048 | 5.9236       |
| 313.15 | 1.14395    | 49.7       | 1.5038 | 5.9414       |
| 318.15 | 1.14049    | 49.3       | 1.5019 | 5.9595       |
| 323.15 | 1.13703    | 48.8       | 1.5004 | 5.9776       |
| 328.15 | 1.13365    | 48.4       | 1.4991 | 5.9954       |

Figure 1. Density (ρ), surface tension (γ), and refractive index (nD) plotted against water content (w_2) at various temperatures (T) for [C_1OC_2mim][Ala] (a,c,e, respectively) and for [C_2OC_2mim][Ala] (b,d,f, respectively). □ 288.15 K; ▲ 293.15 K; ▲ 298.15 K; ▽ 303.15 K; ▶ 308.15 K; ▼ 313.15 K; ▼ 318.15 K; ● 323.15 K; ★ 328.15 K.
Table 1. Cont.

| T (K) | ρ (g cm⁻³) | γ (mJ m⁻²) | nD | α (K⁻¹ × 10⁴) |
|-------|------------|------------|-----|--------------|
|       | [C₂OC₂mim][Ala] |           |     |              |
| 288.15 | 1.13849    | 49.6       | 1.4942 | 5.8490       |
| 293.15 | 1.13475    | 49.3       | 1.4927 | 5.8683       |
| 298.15 | 1.13190    | 48.9       | 1.4914 | 5.8880       |
| 303.15 | 1.12854    | 48.5       | 1.4899 | 5.9005       |
| 308.15 | 1.12514    | 48.0       | 1.4885 | 5.9184       |
| 313.15 | 1.12175    | 47.6       | 1.4869 | 5.9363       |
| 318.15 | 1.11521    | 46.7       | 1.4839 | 5.9711       |
| 323.15 | 1.11166    | 46.3       | 1.4824 | 5.9901       |
| 328.15 | 1.10866    | 45.9       | 1.4809 | 6.0061       |

Standard uncertainties (u) are u(T) = 0.02 K and u(ρ) = 10 kPa; expanded uncertainties (U) are u(ρ) = 0.002 g cm⁻³, U(γ) = 0.3 mJ m⁻², and U(n_D) = 0.003, with 95% confidence (k = 2).

2.2. Strength of [CₙOC₂mim][Ala] (n = 1, 2) Intermolecular Interactions

The density of ILs increases gradually as temperature rises. At higher temperatures, the mobility of constituent ions improves and the unit volume increases [31]. The thermal expansion coefficient (α) is defined as

\[ α = (1/V)(\partial V/\partial Y)_p = −(\partial \ln \rho/\partial T)_p \]  

where V is molar volume. Molar volume is defined as

\[ V = M/ρ \]  

The molecular volume \( V_m \) is defined as

\[ V_m = M/Nρ = V/N \]  

where N is the Avogadro constant, V is molar volume, and M is molar mass.

At 298.15 K, \( V_m \) is 0.3300 nm³ for [C₁OC₂mim][Ala] and 0.3571 nm³ for [C₂OC₂mim][Ala] (Table S4). The difference between these indicates that the contribution of methylene (-CH₂-) to \( V_m \) is 0.0271 nm³. This is close to the average contribution methylene makes to the \( V_m \) of several other ILs listed in Table S5 (0.0278 nm³).

Lattice energy (\( U_{POT} \)) and standard entropy (\( S^0_{298} \)) can be calculated according to Glasser’s theory; Equation (4) is suitable for MX(1:1) type ionic salts. The constants in Equation (5) are empirical values [32].

\[ U_{POT} = 1981.2 (\rho/M)^{1/3} + 103.8 \]  

\[ S^0_{298} = 1246.5V/m + 29.5 \]  

\( U_{POT} \) reflects the strength of intermolecular interactions and can be used to measure the stability of ILs [32,33]. \( U_{POT} \) is 443 kJ mol⁻¹ for [C₁OC₂mim][Ala] and 435 kJ mol⁻¹ for [C₂OC₂mim][Ala], implying that methylene’s average contribution to \( U_{POT} \) is −8 kJ mol⁻¹. \( U_{POT} \) is inversely related to molar volume. Addition of a methylene group will reduce the ionic or molecular packing efficiency, decreasing the strength of the interactions.

To some extent, standard entropy reflects the degree of disorder of molecular arrangements [33]. \( S^0_{298} \) is 441 J K⁻¹ mol⁻¹ for [C₁OC₂mim][Ala] and 475 J K⁻¹ mol⁻¹ for [C₂OC₂mim][Ala], suggesting that methylene’s average contribution to \( S^0_{298} \) is 34 J K⁻¹ mol⁻¹ (Table S5). This indicates that ILs with longer aliphatic chains are more disordered. Standard entropy increases as molecular volume increases. \( S^0_{298} \) of ILs is usually greater than 200 J K⁻¹ mol⁻¹, compared with the more molecularly ordered conventional inorganic salts such as NaCl (72.1 J K⁻¹ mol⁻¹) and KCl (82.6 J K⁻¹ mol⁻¹) [34]. This may explain why ILs are molten below 373 K.
The association enthalpy ($\Delta_A H_m^0$) also reflects the strength of intermolecular interactions: the higher the $\Delta_A H_m^0$, the stronger the gaseous state interactions. $\Delta_A H_m^0$ of ILs in the gaseous phase can be calculated based on the thermodynamic cycle shown in Scheme 1 [29].

$$M'(g) + X(g) \rightarrow [MX]^0(g)$$

Scheme 1. Thermodynamic cycle for calculating $\Delta_A H_m^0$.

Vaporization enthalpy ($\Delta_0^s H_m^0$) is a key parameter for calculating $\Delta_A H_m^0$. It is estimated from Equation (6):

$$g_s = a + b \left( \Delta_0^s H_m^0 - RT \right)$$  \hspace{1cm} (6)

where $g_s$ is the molar surface Gibbs energy; $\gamma$ is surface tension; $V$ is molar volume; $N$ is the Avogadro constant; $\Delta_0^s H_m^0$ is vaporization enthalpy; $R$ is the gas constant; $T$ is temperature; and $a$ and $b$ are the empirical constants $-1.519 \text{ kJ/mol}^{-1}$ and $0.09991$, respectively [29].

The estimated vaporization enthalpy is $164.1 \text{ kJ/mol}^{-1}$ for $[C_1OC_2mim][Ala]$ and $165.1 \text{ kJ/mol}^{-1}$ for $[C_2OC_2mim][Ala]$. Consequently, $\Delta_A H_m^0$ is $-278.9 \text{ kJ/mol}^{-1}$ for $[C_1OC_2mim][Ala]$ and $-269.9 \text{ kJ/mol}^{-1}$ for $[C_2OC_2mim][Ala]$. The $\Delta_A H_m^0$ of other ILs are listed in Table S5. Again, addition of methylene reduces packing efficiency and increases the degree of molecular disorder. Thus, for ILs with the same anions, the absolute value of $\Delta_A H_m^0$ decreases as the length of the imidazole ring alkyl side chains increases. For ILs with the same cations, $\Delta_A H_m^0$ decreases with increasing anion volume.

2.3. Prediction of Surface Tension Based on Molar Surface Gibbs Energy

The parameter $g_s$ used to estimate vaporization enthalpy was developed in our previous work by modifying Li’s model [35]. The definition of $g_s$ is consistent with the concept presented by Myers [36]. Thus, $g_s$ is a true thermodynamic function that integrates volumetric and surface properties.

Plotting $g_s$ against $T$ for $[C_nOC_2mim][Ala](n = 1, 2)$ yields straight lines (Figure 2) such that their relationship can be expressed as

$$g_s = G_0 - G_1 T$$  \hspace{1cm} (8)

![Figure 2. Molar surface Gibbs energy ($g_s$) plotted against temperature ($T$). ▲ [C_1OC_2mim][Ala]: $g_s = 19,803 - 17.39T$, $r^2 = 0.995$, sd = 16.4; ● [C_2OC_2mim][Ala]: $g_s = 20,658 - 19.94T$, $r^2 = 0.996$, sd = 17.5.](image-url)
G₀ and G₁ for [CₙOC₂mim][Ala](n = 1, 2) are obtained from Figure 2 and substituted into Equation (8) to give the estimated molar surface Gibbs energy, $g_{s(est)}$. Values of $g_s$, G₀, G₁, and $g_{s(est)}$ are listed in Table 2.

### Table 2. Molar surface Gibbs energy ($g_s$), G₀, G₁, and estimated molar surface Gibbs energy ($g_{s(est)}$) for [CₙOC₂mim][Ala](n = 1, 2).

| T (K) | $g_s$ (kJ mol⁻¹) | G₀ | G₁ | $g_{s(est)}$ (kJ mol⁻¹) |
|-------|-----------------|----|----|-------------------------|
|       | [C₁OC₂mim][Ala] |    |    |                         |
| 288.15| 14.78           | 19,803 | 17.4 | 14.79                   |
| 293.15| 14.69           | 19,803 | 17.4 | 14.70                   |
| 298.15| 14.63           | 19,803 | 17.4 | 14.62                   |
| 303.15| 14.55           | 19,803 | 17.4 | 14.53                   |
| 308.15| 14.43           | 19,803 | 17.4 | 14.44                   |
| 313.15| 14.37           | 19,803 | 17.4 | 14.35                   |
| 318.15| 14.29           | 19,803 | 17.4 | 14.27                   |
| 323.15| 14.17           | 19,803 | 17.4 | 14.18                   |
| 328.15| 14.08           | 19,803 | 17.4 | 14.09                   |
|       | [C₂OC₂mim][Ala] |    |    |                         |
| 288.15| 14.88           | 20,658 | 19.9 | 14.92                   |
| 293.15| 14.82           | 20,658 | 19.9 | 14.82                   |
| 298.15| 14.73           | 20,658 | 19.9 | 14.72                   |
| 303.15| 14.63           | 20,658 | 19.9 | 14.63                   |
| 308.15| 14.51           | 20,658 | 19.9 | 14.53                   |
| 313.15| 14.42           | 20,658 | 19.9 | 14.43                   |
| 318.15| 14.33           | 20,658 | 19.9 | 14.33                   |
| 323.15| 14.20           | 20,658 | 19.9 | 14.23                   |
| 328.15| 14.11           | 20,658 | 19.9 | 14.13                   |

The Lorentz-Lorenz equation expresses the relationship between $n_D$ and the mean molecular polarizability ($\alpha_p$) [37]:

$$R_m = \left[\frac{(n_D^2 - 1)}{(n_D^2 + 2)}\right] \cdot V = \left(\frac{4\pi N}{3}\right) \cdot \alpha_p$$

(9)

where $R_m$ is molar refraction, $\alpha_p$ is mean molecular polarizability, and $n_D$ is refractive index. This has been combined with $g_s$ to give an improved Lorentz-Lorenz equation [38] that can predict surface tension, $\gamma_{(est)}$:  

$$\gamma_{(est)}^{3/2} = \frac{\left[g_{s(est)}^{3/2} / N^{1/2} R_m\right] (n_D^2 - 1)}{(n_D^2 + 2)}$$

(10)

The $R_m$, $\alpha_p$, and $\gamma_{(est)}$ for [CₙOC₂mim][Ala](n = 1, 2) are listed in Table 3. Plotting estimated surface tension values against their corresponding experimental values produces a straight line (Figure 3). A similar plot for other ionic and molecular liquids also illustrates a linear relationship (Table S6, Figure 4), showing that this method is applicable for the surface tension prediction of both types of liquid.
Table 3. Molar refraction ($R_m$), mean molecular polarizability ($\alpha_p$), and estimated surface tension ($\gamma_{est}$) of $[C_nOC_2\text{mim}][\text{Ala}] (n = 1, 2)$.

| $T$ (K) | $R_m$ | $\alpha_p \times 10^{24}$ | $\gamma_{est}$ |
|---------|-------|----------------|---------------|
| 288.15  | 57.74 | 22.91 | 51.6          |
| 293.15  | 57.77 | 22.92 | 51.2          |
| 298.15  | 57.76 | 22.92 | 50.8          |
| 303.15  | 57.80 | 22.93 | 50.4          |
| 308.15  | 57.82 | 22.94 | 50.0          |
| 313.15  | 57.84 | 22.95 | 49.6          |
| 318.15  | 57.89 | 22.97 | 49.2          |
| 323.15  | 57.90 | 22.97 | 48.8          |
| 328.15  | 57.89 | 22.97 | 48.4          |

| $T$ (K) | $R_m$ | $\alpha_p \times 10^{24}$ | $\gamma_{est}$ |
|---------|-------|----------------|---------------|
| 288.15  | 62.24 | 24.69 | 49.4          |
| 293.15  | 62.28 | 24.71 | 49.0          |
| 298.15  | 62.30 | 24.72 | 48.6          |
| 303.15  | 62.32 | 24.73 | 48.2          |
| 308.15  | 62.36 | 24.74 | 47.7          |
| 313.15  | 62.37 | 24.75 | 47.3          |
| 318.15  | 62.39 | 24.76 | 46.9          |
| 323.15  | 62.41 | 24.76 | 46.5          |
| 328.15  | 62.43 | 24.77 | 46.1          |

Figure 3. Plot of surface tension $\gamma_{est}$ against $\gamma_{exp}$ for $[C_nOC_2\text{mim}][\text{Ala}] (n = 1, 2)$. $\gamma_{est} = 1.0581\gamma_{exp} - 2.9851; r^2 = 0.995; sd = 0.11$.

Figure 4. Plot of surface tension $\gamma_{est}$ against $\gamma_{exp}$ for various ionic and molecular liquids (see Table S6). $\gamma_{est} = 1.0009\gamma_{exp} - 0.03643; r^2 = 0.999; sd = 0.10$.

For ILs sharing the same anions (Table 1 and Table S6), $n_D$ decreases as the length of the alkyl chain in the cations increases. Refractive index correlates with dipole moment [39,40].
which increases with higher molecular packing density [41]. Thus, a larger dipole moment results in a higher refractive index. The $n_D$ is larger in $[\text{C}_1\text{OC}_2\text{mim}][\text{Ala}]$ than $[\text{C}_2\text{OC}_2\text{mim}][\text{Ala}]$, so the packing density of the former is higher, which is consistent with the density trend of the two ILs.

As polarizability increases, Coulomb interactions are reduced and ion mobility rises [42]. The $\alpha_p$ of $[\text{C}_1\text{OC}_2\text{mim}][\text{Ala}]$ is lower than $[\text{C}_2\text{OC}_2\text{mim}][\text{Ala}]$, so its Coulomb interactions are stronger. This finding is similar to the pattern observed for $U_{\text{POT}}$ and $\Delta AH_m^0$.

2.4. Molar Surface Entropy: Polarity Contribution from Surface Liquid

For most liquids, surface tension declines as temperature increases, as shown by the Eötvös equation:

$$\gamma V^{2/3} = k(T_c - T) \quad (11)$$

where $T_c$ is critical temperature and $k$ is the Eötvös equation parameter, which is associated with polarity. For some organic liquids with weak polarity, $k$ is nearly $2.2 \times 10^{-7} \text{ J mol}^{-2/3} \text{ K}^{-1}$, while for some with strong polarity, such as molten NaCl, it is nearly $0.4 \times 10^{-7} \text{ J mol}^{-2/3} \text{ K}^{-1}$ [35,43]. However, the physical significance of $k$ is not clear. Multiplying both sides of the Eötvös equation by $N^{1/3}$ [35] gives

$$g_s = C_0 - C_1 T \quad (12)$$

which fits the fundamental thermodynamic concept:

$$G = H - TS \quad (13)$$

$C_1$ denotes the molar surface entropy and is given by $C_1 = -(\frac{\partial g_s}{\partial T})_p$.

The relationship between molar surface entropy (defined here as $s$ [29]) and $k$ is expressed as

$$s = N^{1/3}k \quad (14)$$

Entropy is directly linked to the number of microstates [44]. Higher entropy means molecules can be arranged in more ways, while the total energy remains constant. Thus, the physical significance of $s$ is clear—it reflects the polarity of a liquid’s surface (higher $s$, lower surface polarity). The value of $s$ is 17.39 J mol$^{-1}$ K$^{-1}$ for $[\text{C}_1\text{OC}_2\text{mim}][\text{Ala}]$ and 19.94 J mol$^{-1}$ K$^{-1}$ for $[\text{C}_2\text{OC}_2\text{mim}][\text{Ala}]$. Values for other EFILs are listed in Table 4. The overall trend is that for ILs with the same cations, such as $[\text{C}_1\text{OC}_2\text{mim}]^+,[\text{C}_2\text{OC}_2\text{mim}]^+$, and $[\text{C}_1\text{OC}_4\text{mim}]^+$, $s$ increases as the volume of anions increases. Cl$^-$, [Ala]$^-$, [Thr]$^-$, and [Gly]$^-$ clearly obey this rule. It can be speculated that larger anions cause greater disordering of surface molecules, leading to lower polarity. However, [NTf$_2$]$^-$ does not conform to this rule. This may be due to it being more symmetrical than other anions, facilitating a more orderly arrangement of surface molecules and increasing the polarity. For ILs sharing the same anions, the general trend is that $s$ increases as the volume of cations increases. Values of $s$ for different other ILs (Table S7) confirm this effect.

| IL                     | $s$ (J mol$^{-1}$ K$^{-1}$) | $V \times 10^4$ (m$^3$ mol$^{-1}$) |
|------------------------|-----------------------------|-----------------------------------|
| $[\text{C}_1\text{OC}_2\text{mim}]\text{Cl}$ [38] | 15.99                       | 1.52                             |
| $[\text{C}_1\text{OC}_2\text{mim}][\text{Ala}]$  | 17.39                       | 1.99                             |
| $[\text{C}_1\text{OC}_2\text{mim}]\text{Thr}$ [43] | 26.60                       | 2.18                             |
| $[\text{C}_1\text{OC}_2\text{mim}][\text{NTf}_2]$ [19] | 17.80                       | 2.80                             |
| $[\text{C}_1\text{OC}_2\text{mim}]\text{Cl}$ [38] | 17.81                       | 1.68                             |
| $[\text{C}_2\text{OC}_2\text{mim}][\text{Ala}]$  | 19.94                       | 2.15                             |
| $[\text{C}_2\text{OC}_2\text{mim}]\text{Thr}$ [43] | 28.12                       | 2.37                             |
| $[\text{C}_2\text{OC}_2\text{mim}][\text{NTf}_2]$ [19] | 19.32                       | 2.99                             |
| $[\text{C}_2\text{OC}_2\text{mim}]\text{Gly}$ [46] | 19.56                       | 2.19                             |
| $[\text{C}_2\text{OC}_2\text{mim}][\text{Ala}]$ [46] | 20.54                       | 2.29                             |
| $[\text{C}_2\text{OC}_2\text{mim}]\text{Thr}$ [46] | 22.082                      | 2.51                             |
| $[\text{C}_2\text{OC}_2\text{mim}][\text{NTf}_2]$ [19] | 18.20                       | 2.81                             |
| $[\text{C}_2\text{OC}_2\text{mim}]\text{Thr}$ [46] | 18.49                       | 2.97                             |
| $[\text{C}_2\text{OC}_2\text{mim}][\text{NTf}_2]$ [19] | 20.57                       | 3.16                             |
Data for [C\textsubscript{1}OC\textsubscript{2}mim][NTf\textsubscript{2}], [C\textsubscript{2}OC\textsubscript{1}mim][NTf\textsubscript{2}], [C\textsubscript{2}OC\textsubscript{2}mim][NTf\textsubscript{2}], and [C\textsubscript{1}OC\textsubscript{3}mim][NTf\textsubscript{2}] (Table 4) imply that, for ILs with the same number of alkyl side chain carbons, the position of the ether group also affects \( s \), presumably because it affects packing efficiency on the liquid surface.

2.5. A New Model for Predicting Polarity

Experimental methods for measuring polarity, such as \( E_T(30) \), are time consuming and laborious. Here, we present a predictive model that establishes a relationship between polarity and the easily determined physicochemical properties of density, surface tension, and refractive index.

Our previous work [28], based on Hildebrand and Scott’s theory [47], proposed \( \delta_\mu \) as a polarity scale. \( \delta_\mu \) is the solubility parameter derived from the contribution of the average permanent dipole moment:

\[
\delta_\mu^2 = \frac{\Delta \delta_1 H_0^{\text{mu}}}{V} - (1 - x)RT/V
\]  

where \( V \) is the molar volume and \( \Delta \delta_1 H_0^{\text{mu}} \) is the contribution of the average permanent dipole moment to \( \Delta \delta_1 H_0^{\text{m}} \), such that

\[
\Delta \delta_1 H_0^{\text{mu}} = \Delta \delta_1 H_0^{\text{m}} - \Delta \delta_1 H_0^{\text{mn}}
\]  

where \( \Delta \delta_1 H_0^{\text{mn}} \) is the contribution of the induced dipole moment to \( \Delta \delta_1 H_0^{\text{m}} \) and can be calculated from the Lawson–Ingham equation [48]:

\[
\Delta \delta_1 H_0^{\text{mn}} = C \left[ \left( \eta D_2 - 1 \right) / (\eta D_2 + 2) \right] V = C R m
\]  

where \( C \) is the empirical constant 1.297 kJ·cm\(^{-3}\). In Equation (15), \( x \) represents \( \Delta \delta_1 H_0^{\text{mn}} / \Delta \delta_1 H_0^{\text{m}} \) (at 298.15 K). The \( \delta_\mu \) polarity of [C\textsubscript{4}mim][Ala] (21.03 J\(^{1/2}\)·cm\(^{-3/2}\)) is larger than [C\textsubscript{2}OC\textsubscript{2}mim][Ala] (19.65 J\(^{1/2}\)·cm\(^{-3/2}\)). However, there is an obvious drawback to \( \delta_\mu \): it has a dimension (J\(^{1/2}\)·cm\(^{-3/2}\)), while some polarity scales, such as the dielectric constant, are non-dimensional. Furthermore, the contribution of the induced dipole moment was neglected. Therefore, \( \delta_\mu \) was improved as follows and designated as \( P [45] \):

\[
P = \frac{\delta_\mu}{\delta_n} = \left[ \frac{\Delta \delta_1 H_0^{\text{mu}} / V - (1 - x)RT/V}{\Delta \delta_1 H_0^{\text{mn}} / V - xRT/V} \right]^{1/2}
\]  

where \( \delta_n \) is the solubility parameter from the contribution of the induced dipole moment. Comparison of \( \Delta \delta_1 H_0^{\text{mu}} \) and \( \Delta \delta_1 H_0^{\text{mn}} \) shows that \((1-x)RT/V \) and \( xRT/V \) can be omitted and Equation (18) can be expressed as

\[
P = \left( \frac{\Delta \delta_1 H_0^{\text{mu}} / \Delta \delta_1 H_0^{\text{mn}}} \right)^{1/2}
\]  

The effects of average permanent dipole moment and induced dipole moment are both considered within \( P \), which is dimensionless, with a large value indicating high polarity. [C\textsubscript{4}mim][BF\textsubscript{4}] is hydrophilic and [C\textsubscript{4}mim][NTf\textsubscript{2}] is hydrophobic. According to Seddon et al. [49], \( P \) is 1.226 for [C\textsubscript{4}mim][BF\textsubscript{4}] and 0.401 for [C\textsubscript{4}mim][NTf\textsubscript{2}]. This higher polarity of [C\textsubscript{4}mim][BF\textsubscript{4}] fits practical experience. Thus, the parameter \( P \) is capable of measuring the polarity of ILs. \( P \) is 1.191 for [C\textsubscript{1}OC\textsubscript{2}mim][Ala] and 1.043 for [C\textsubscript{2}OC\textsubscript{2}mim][Ala].
This study divided polarity into two compartments: the contribution from the body of a liquid, and the contribution from the surface. Cohesive energy density can demonstrate the strength of intermolecular interactions within the body [48]. \( \delta_{\mu}^2 \) is the cohesive energy density from the average permanent dipole moment and \( \delta_{n}^2 \) is from the induced dipole moment. Consequently, \( P^2 \) can describe the polarity of the body of a liquid:

\[
P^2 = \frac{\delta_{\mu}^2}{\delta_{n}^2}
\]  

Molar surface entropy (s) was proven above to reflect the polarity of a liquid surface. Combining s and \( P^2 \), a new polarity scale, \( P_N \), is now proposed:

\[
P_N = \frac{s}{P^2} = \frac{s}{\left( \frac{\delta_{\mu}^2}{\delta_{n}^2} \right)}
\]  

This compartmentalized scale is a novel method to evaluate polarity, with a large \( P_N \) indicating weak polarity. Based on literature data [50–55], \( P_N \) is 22.03 J·mol\(^{-1}\)·K\(^{-1}\) for [C\(_4\)mim][NTf\(_2\)] and 14.50 J·mol\(^{-1}\)·K\(^{-1}\) for [C\(_4\)mim][BF\(_4\)]. These results fit with practical experience and demonstrate the rationality of the \( P_N \) scale. The \( P_N \) of various ether-functionalized ILs are listed in Table 5. For ILs with the same anion, \( P_N \) declines as the length of the imidazole ring alkyl side chain increases. This trend supports the contention that the strength of intermolecular interactions and the degree of disorder of molecular arrangements influence polarity.

Table 5. Polarity of various ether-functionalized ionic liquids using the new \( P_N \) scale.

| IL               | \( P_N \) (J·mol\(^{-1}\)·K\(^{-1}\)) | Reference |
|------------------|-----------------------------------|-----------|
| [COC\(_2\)mim][Cl] | 12.86                             | [37]      |
| [C\(_2\)OC\(_2\)mim][Cl] | 16.76                           | [37]      |
| [C\(_4\)OC\(_2\)mim][Ala] | 12.26                           | This work |
| [C\(_2\)OC\(_2\)mim][Ala] | 18.33                           | This work |
| [COC\(_2\)mim][Ala]         | 21.83                           | [39]      |
| [COC\(_2\)mim][Thr]         | 22.18                           | [38]      |
| [C\(_2\)OC\(_2\)mim][Thr]  | 25.46                           | [38]      |
| [COC\(_4\)mim][Thr]         | 24.52                           | [39]      |
| [CO\(_2\)C\(_2\)mim][NTf\(_2\)] | 31.31                         | [13]      |
| [C\(_2\)OC\(_2\)mim][NTf\(_2\)] | 35.40                        | [13]      |
| [C\(_3\)OC\(_2\)mim][NTf\(_2\)] | 35.57                        | [13]      |
| [C\(_2\)OC\(_2\)mim][NTf\(_2\)] | 42.66                        | [13]      |
| [C\(_2\)OC\(_2\)mim][NTf\(_2\)] | 55.1                          | [13]      |
| [COC\(_4\)mim][Gly]         | 19.64                           | [39]      |

The \( P_N \) scale can be validated by comparison with other polarity scales (Table 6). FTIR spectroscopy probes [56] and \( E_T \) [57] show that the polarity of [C\(_2\)mim][BF\(_4\)] is larger than [C\(_4\)mim][BF\(_4\)]. The \( P_N \) scale gives the same qualitative result. Wu et al. determined the order of polarity of several ILs to be [C\(_4\)mim][BF\(_4\)] > [C\(_4\)mim][NTf\(_2\)] > [C\(_4\)mim][OAc] using \( E_T \) [58]. Again, \( P_N \) gives the same result.
Table 6. Polarity of various ionic liquids estimated using the $P_N$ scale.

| IL                  | $P_N$ (J mol$^{-1}$ K$^{-1}$) |
|---------------------|-------------------------------|
| [C$_6$mim]OAC       | 35.73                         |
| [C$_4$mim]OAC       | 23.24                         |
| [C$_4$mim]NTf$_2$ [51,53] | 22.03                     |
| [C$_4$mim]NTf$_2$   | 19.96                         |
| [C$_4$mim]BF$_4$    | 14.50                         |
| [C$_2$mmim]NTf$_2$  | 14.01                         |
| [C$_5$mim]Lact      | 12.87                         |
| [C$_2$mim]BF$_4$    | 8.24                          |
| [C$_2$mim]Lact      | 8.16                          |

Furthermore, when $P_N$ is applied to molecular liquids, the estimated polarity is broadly, and inversely, consistent with the dielectric constant $\varepsilon$ [59] (Table 7). The correlation between $P_N$ and the inverse $\varepsilon^{-1}$ (Figure 5) is $r^2 = 0.94$, demonstrating that $P_N$ is also suitable for molecular liquids.

Table 7. $P_N$ and dielectric constant ($\varepsilon$) of various molecular liquids.

| Molecular Liquid    | $P_N$  | $\varepsilon$ |
|---------------------|--------|---------------|
| Ethyl acetate       | 169.14 | 6.1           |
| Chloroform          | 167.19 | 4.8           |
| Tetrahydrofuran     | 124.29 | 7.5           |
| Pyridine            | 60.64  | 12.3          |
| Benzyl alcohol      | 48.13  | 13.0          |
| 1-Hexanol           | 27.06  | 13.0          |
| Cyclohexanol        | 25.09  | 15.0          |
| 1-Propanol          | 8.48   | 20.3          |
| Ethanol             | 5.52   | 28.3          |
| Methanol            | 2.40   | 33.0          |

Figure 5. Inverse of the dielectric constant ($\varepsilon^{-1}$) of various molecular liquids plotted against the estimated polarity $P_N$. Linear correlation coefficient ($r^2$) 0.94.
$E_T(30)$ is one of the most popular polarity scales for evaluating ILs, but it is laborious and costly [60]. Moreover, the results vary depending on the molecular probe used [61]. However, using $P_N$, polarity can be determined simply from density, surface tension, and refractive index. The dielectric constant is the traditional polarity scale for organic solvents. The comparison of dielectric constant and $P_N$ proves the universal applicability of $P_N$. Thus, this new $P_N$ scale is demonstrated to be a viable predictive method for evaluating the polarity of both ionic and molecular liquids based on easily measured physicochemical properties. It will find applications in many fields, particular those employing novel ionic liquids for which the evaluation of polarity is expensive and time consuming.

3. Materials and Methods

3.1. Materials

The sources and purity of reagents are listed in Table 8. N-Methylimidazole (AR grade) was purified by distillation, while 2-chloroethyl methyl ether and 2-chloroethyl ethyl ether (both AR grade) were used as purchased. DL-Alanine was recrystallized from water and dried in a vacuum oven [62].

Table 8. Source and purity of reagents.

| Reagent Name          | CAS No.   | Source | Purification                  | Mass Fraction Purity | Analysis               |
|-----------------------|-----------|--------|-------------------------------|----------------------|------------------------|
| Anion exchange resin  | 717       | SRC    | None                          | Granularity > 0.950  | GC                     |
| N-Methylimidazole     | 616-47-7  | ACROS  | Distillation                  | >0.990               | FM                     |
| 2-Chloroethyl methyl   | 627-42-9  | SRC    | None                          | >0.995               | FM                     |
| 2-Chloroethyl ethyl    | 628-34-2  | SRC    | None                          | >0.995               | FM                     |
| Ethyl acetate         | 141-78-6  | SRC    | None                          | >0.995               | FM                     |
| Anhydrous ethanol      | 64-17-5   | SRC    | None                          | >0.995               | FM                     |
| Sodium hydroxide       | 1310-73-2 | SRC    | None                          | >0.960               | FM                     |
| [C$_n$OC$_2$ mim][Ala] | -         | Synthesis | Solvent extraction, vacuum drying | >0.990 | $^1$H, $^{13}$C NMR |
| [C$_2$OC$_2$ mim][Ala] | -         | Synthesis | Solvent extraction, vacuum drying | >0.990 | $^1$H, $^{13}$C NMR |

FM—Fractional melting; SRC—Shanghai Reagent Co., Ltd.

3.2. Preparation of ILs [C$_n$OC$_2$ mim][Ala]($n = 1, 2$)

[C$_n$OC$_2$ mim][Ala]($n = 1, 2$) were prepared by Fukumoto’s neutralization method [12], and [C$_n$OC$_2$ mim]Cl($n = 1, 2$) by Sheldon’s method [63]. An equal molar amount of 2-chloroethyl methyl ether or 2-chloroethyl ethyl ether was added dropwise to N-methylimidazole under nitrogen in a three-necked round-bottom flask while stirring at 298.15 K. The reaction temperature reached 353.15 K with 2-chloroethyl methyl ether and 373.15 K with 2-chloroethyl ethyl ether. The reactions lasted for 48 h and produced light yellow liquids, which were then washed three times with ethyl acetate, producing [C$_n$OC$_2$ mim]Cl($n = 1, 2$). These were transformed into [C$_n$OC$_2$ mim]OH($n = 1, 2$) using basic anion exchange resin conditioned with sodium hydroxide [29]. The aqueous [C$_n$OC$_2$ mim]OH($n = 1, 2$) were then added dropwise (at slight excess) to aqueous DL-alanine and reacted for 72 h, yielding [C$_n$OC$_2$ mim][Ala]($n = 1, 2$). Water was removed by rotary evaporation and excess DL-alanine by ethanol:acetonitrile (9:1). The solvents were evaporated under reduced pressure and [C$_n$OC$_2$ mim][Ala]($n = 1, 2$) were dried in a vacuum oven for 60 h at 353.15 K. The chemical structures of [C$_n$OC$_2$ mim][Ala]($n = 1, 2$) are shown in Figure 6.
Figure 6. Chemical structures of ionic liquids \([C_nOC_{2mim}]\text{[Ala]}(n = 1, 2)\).

3.3. Analytical Methods

The structures of \([C_nOC_{2mim}]\text{[Ala]}(n = 1, 2)\) were characterized by NMR (Varian XL-300), as shown in the Supplementary Materials. The final water contents (w2) of \([C_nOC_{2mim}]\text{[Ala]}(n = 1, 2)\), as measured using a ZSD-2 Karl Fischer moisture titrator, were 0.00472 and 0.00640 ± 0.0001 (mass fraction), respectively.

Since \([C_nOC_{2mim}]\text{[Ala]}(n = 1, 2)\) form strong hydrogen bonds with water, it is difficult to remove all traces of water from these ILs, which affects their density, surface tension, and refractive index. Therefore, the standard addition method was used to determine these properties. Each parameter was measured in \([C_nOC_{2mim}]\text{[Ala]}(n = 1, 2)\) at different water contents following heating at graduated temperatures. Values were then plotted against water content, and the intercept of the regression lines yielded the parameter values in the anhydrous ILs at a given temperature.

4. Conclusions

\([C_nOC_{2mim}]\text{[Ala]}(n = 1, 2)\) were prepared and their structures confirmed by NMR. Density, surface tension, and refractive index were determined by the standard addition method. Adding methylene to the aliphatic chain of an IL increased its standard entropy. Lattice energy and association enthalpy measurements showed that molecules of \([COC_{2mim}]\text{[Ala]}\) were more compacted, and their intermolecular interactions stronger, than \([C_{2OC_{2mim}}]\text{[Ala]}\). An improved Lorentz-Lorenz equation predicted the surface tension of both ionic and molecular liquids. A new compartmentalized polarity scale \((P_N)\) based on molar surface Gibbs energy and dipole moments is presented. It encompasses the polarity of both the surface and body of a liquid. \([C_{1OC_{2mim}}]\text{[Ala]}\) is shown to have higher polarity than \([C_{2OC_{2mim}}]\text{[Ala]}\) based on \(P_N\). The validity of \(P_N\) is demonstrated by comparison with alternative polarity scales and published polarities of both ionic and molecular liquids.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27103231/s1, Figure S1. \(^1\)H NMR spectrum of IL [COC_{2mim}]\text{[Ala]}; Figure S2. \(^1\)H NMR spectrum of IL \([C_{2OC_{2mim}}]\text{[Ala]}; Figure S3. \(^13\)C NMR spectrum of IL \([COC_{2mim}]\text{[Ala]}; Figure S4. \(^13\)C NMR spectrum of IL \([C_{2OC_{2mim}}]\text{[Ala]}; Table S1. Densities of Ionic Liquids Containing Various Amounts of Water at pressure \(p = 0.1\) MPa; Table S2. Surface Tensions of Ionic Liquids Containing Various Amounts of Water at pressure \(p = 0.1\) MPa; Table S3. Refractive Indexes of Ionic Liquids Containing Various Amount of Water at pressure \(p = 0.1\) MPa; Table S4. The values of molar volume, \(V/\text{cm}^3\cdot\text{mol}^{-1}\) and molecular volume, \(V_m/\text{nm}^3\) for the ILs \([C_nOC_{2mim}]\text{[Ala]}(n = 1, 2)\); Table S5. Molecular volume, \(V_m\), standard molar entropy, \(S^0\), lattice energy, \(U_{\text{POT}}\), vaporization enthalpy, \(\Delta H^0_{\text{Vap}}\), association enthalpy, \(\Delta H^0_{\text{as}}\) for some ionic liquids; Table S6. The estimated surface tension, \(\gamma_{(est)}\), experimental surface tension, \(\gamma_{(exp)}\),...
refractive index, $n_D$, experimental density $\rho_{\text{exp}}$, molar surface Gibbs energy, $g_s$, molar refraction, $R_m$, molar volume, $V$ for different ILs and molecular liquids; Table S7. The molar surface entropy, $s$, for some ILs; Density, $\rho$, surface tension, and refractive index, $n_D$ measuring methods; citation of ref. [30,39,43,52,54,55,64–106].

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