

Structure Property Relationships of Protic Ionic Liquids

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Introduction

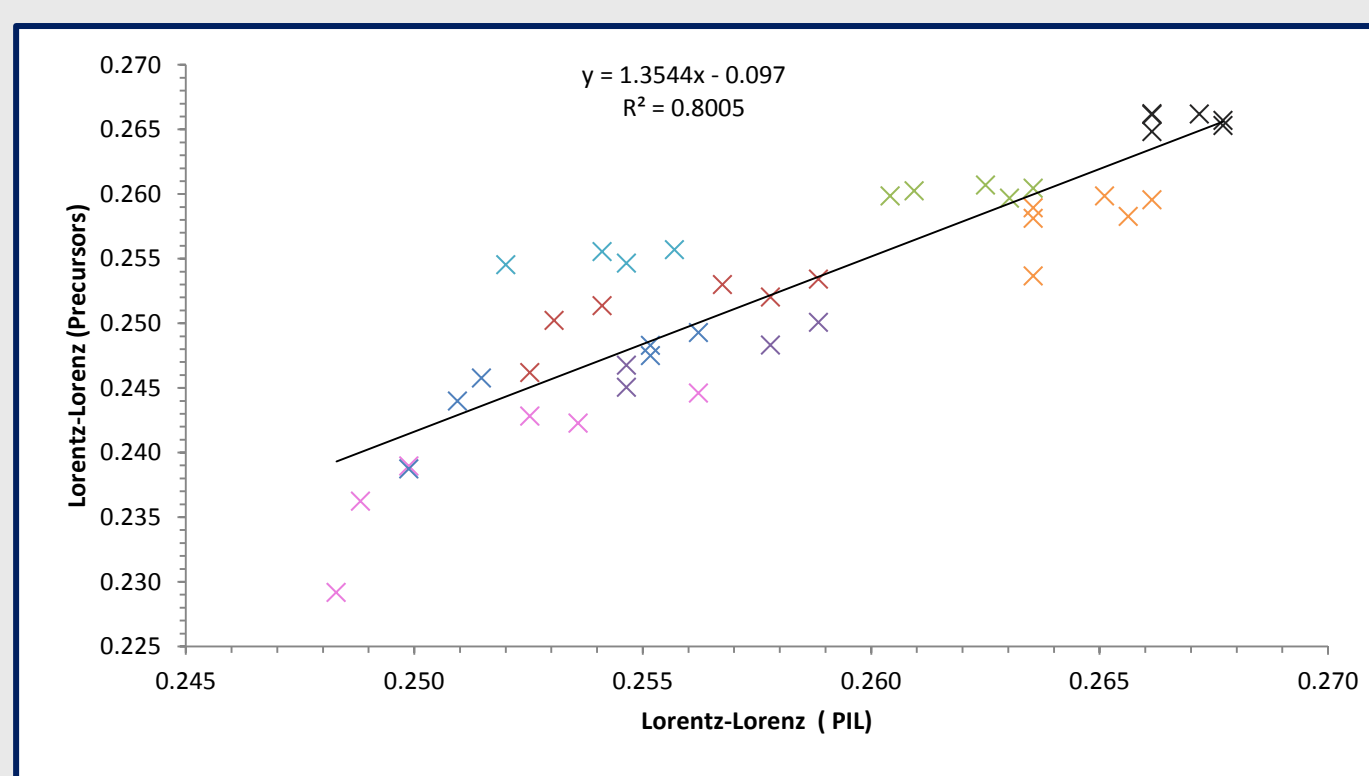
Protic Ionic Liquids (PILs) are cost effective, easy to handle and have similarities in their behaviour to well-understood systems such as surfactants and acid-base mixtures ^[1-3]. The structure-property relationships between precursors and corresponding PILs are still poorly understood. This limits the capability to design new PILs as solvents for new processes or reactions. We have undertaken a comparative study of a range of related PILs on the basis of specific, limited and iterative changes in structure. Physiochemical and solvatochromic properties of each PIL were studied and compared, and trends were derived based on their structural relationships.

Precursors

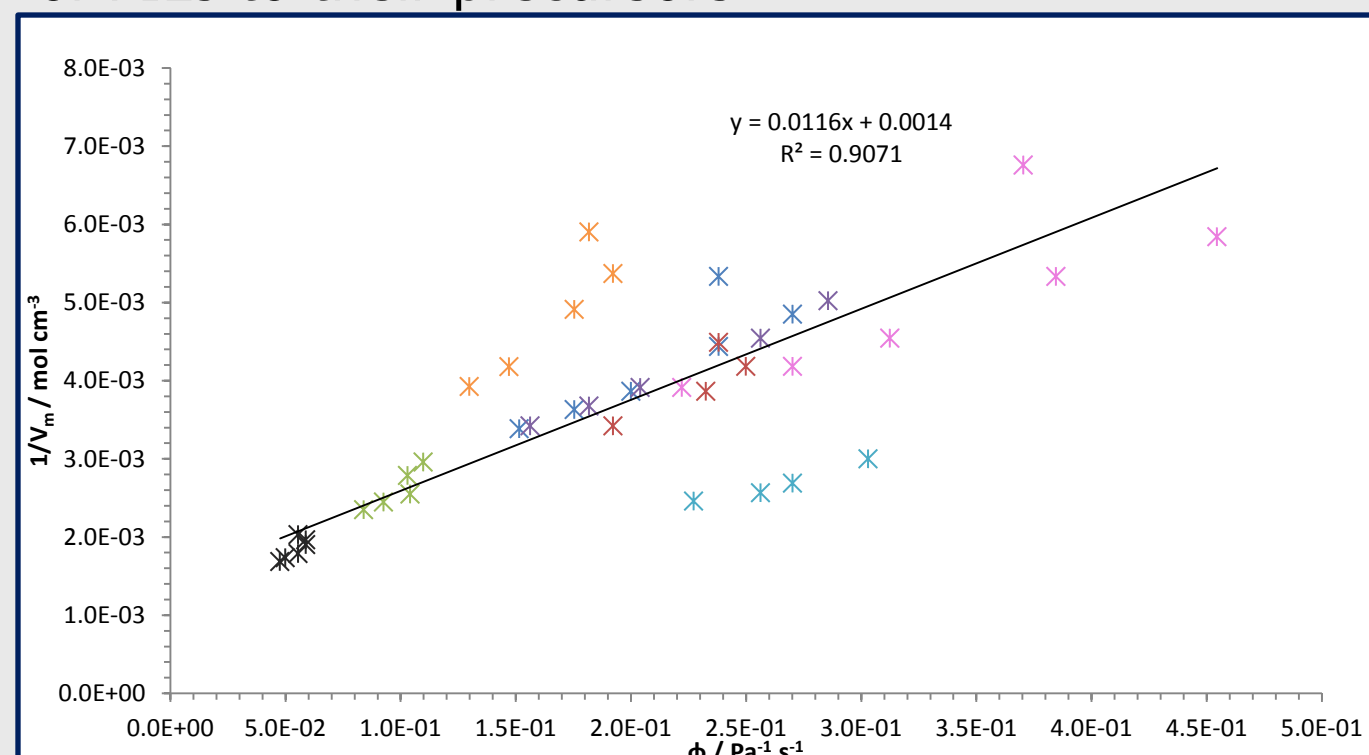
The following precursors were selected to observe the effect of changing the *alkyl* substituents on both the cation and anion. Below is the list of the various anions and cations studied. Only tertiary amines were used due to their stability towards amidation and N-nitrosamine formation.

| Code | Anion Name | pK _{a(aq)} | Code | Cation Name | pK _{a(aq)} | Colour |
|------|------------|---------------------|---|-----------------------------|---------------------|--------|
| 002 | Acetate | 4.74 | ABBC | N,N-Dimethylethylammonium | 10.20 | X |
| 003 | Propanoate | 4.86 | ABBE | N,N-Dimethylbutylammonium | 10.19 | X |
| 004 | Butyrate | 4.81 | ABBN ₂ | N,N-Dimethylhexylammonium | 10.02 | X |
| 006 | Hexanoate | 4.87 | ABBS ₃ | N,N-Dimethyldodecylammonium | 9.97 | X |
| 007 | Heptanoate | 4.89 | ACCC | N,N,N-Triethylammonium | 10.78 | X |
| 008 | Octanoate | 4.89 | AZ ₃ Z ₃ Z ₃ | N,N,N-Triisobutylammonium | 10.30 | X |
| | | | ABCψD | N-Methylpiperidinium | 8.35 | X |
| | | | AP ₂ P ₂ P ₂ | N,N,N-Trioctylammonium | 10.08 | X |

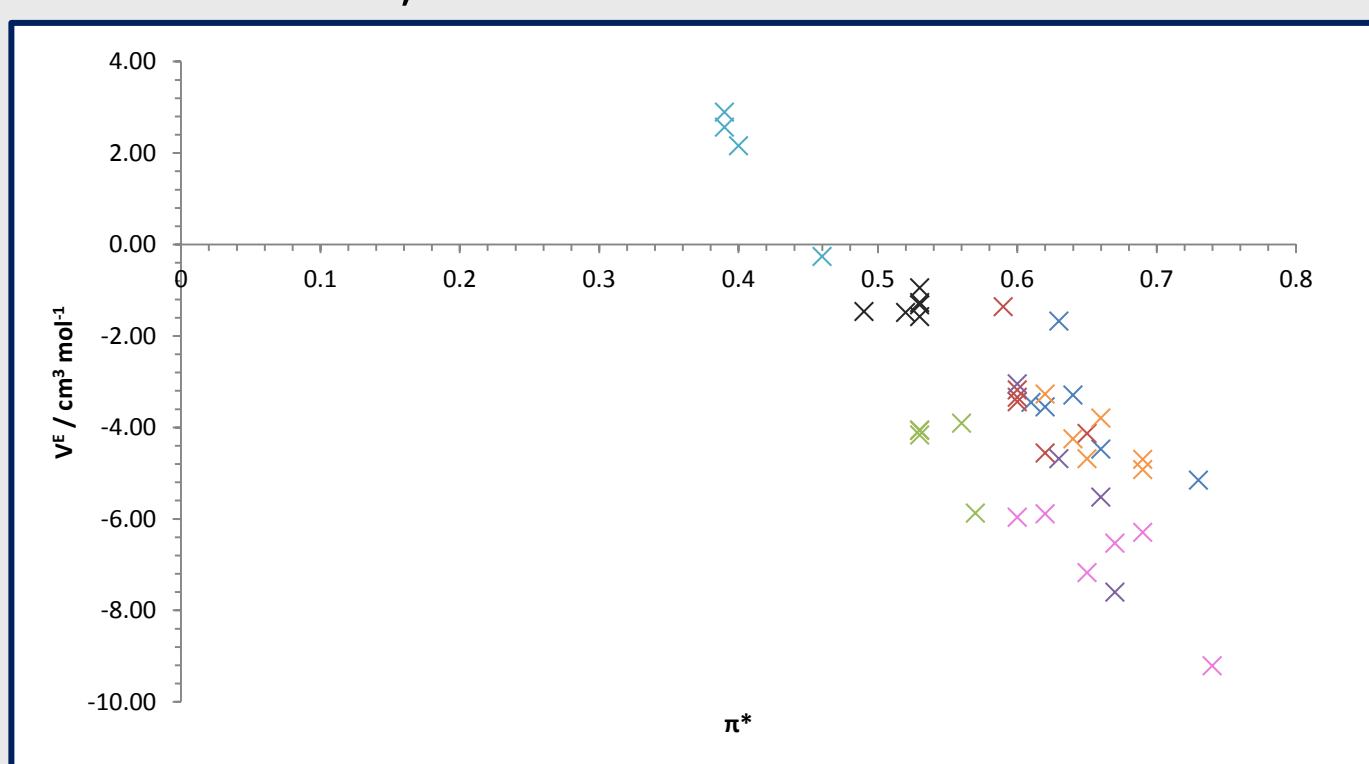
Results



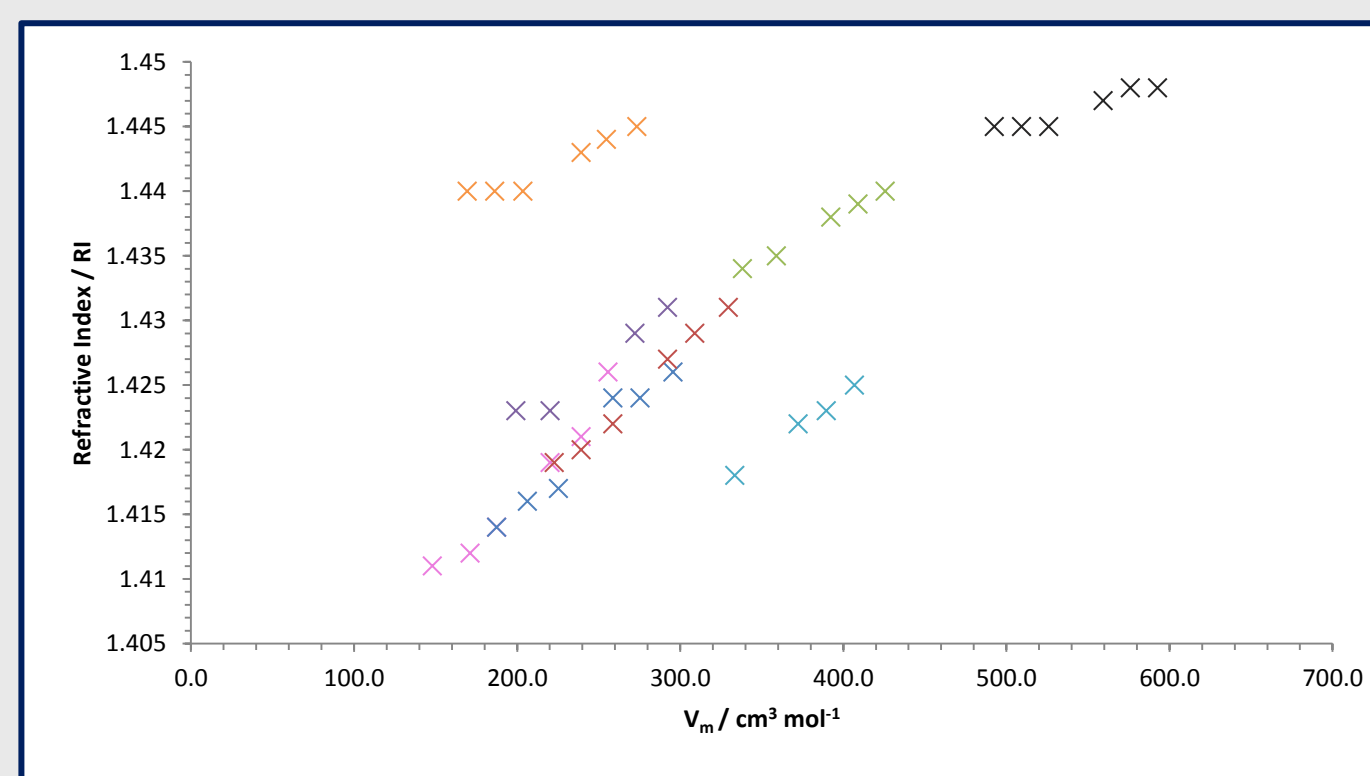
Graph 1: Lorentz-Lorenz plot of refractive indices of PILs to their precursors.



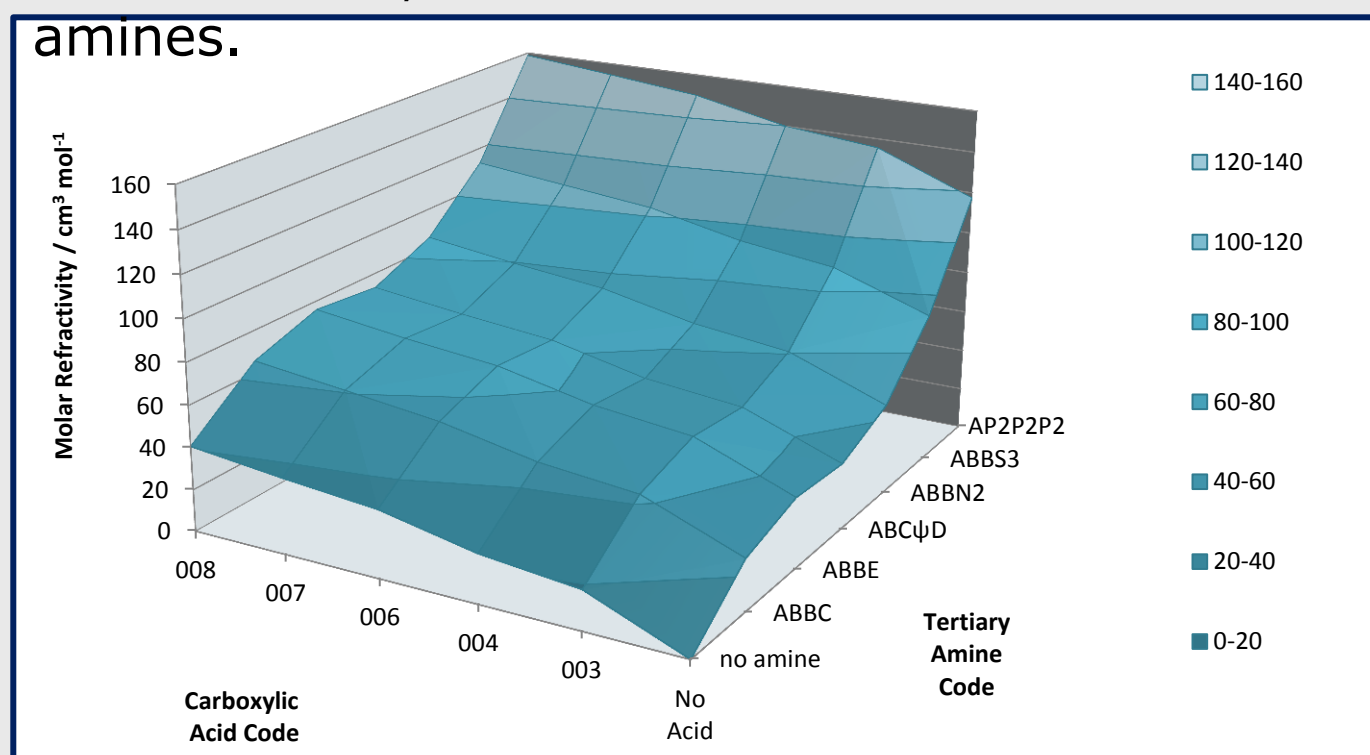
Graph 3: Fluidity is inversely proportional to molar volume, deviations with non linear amines



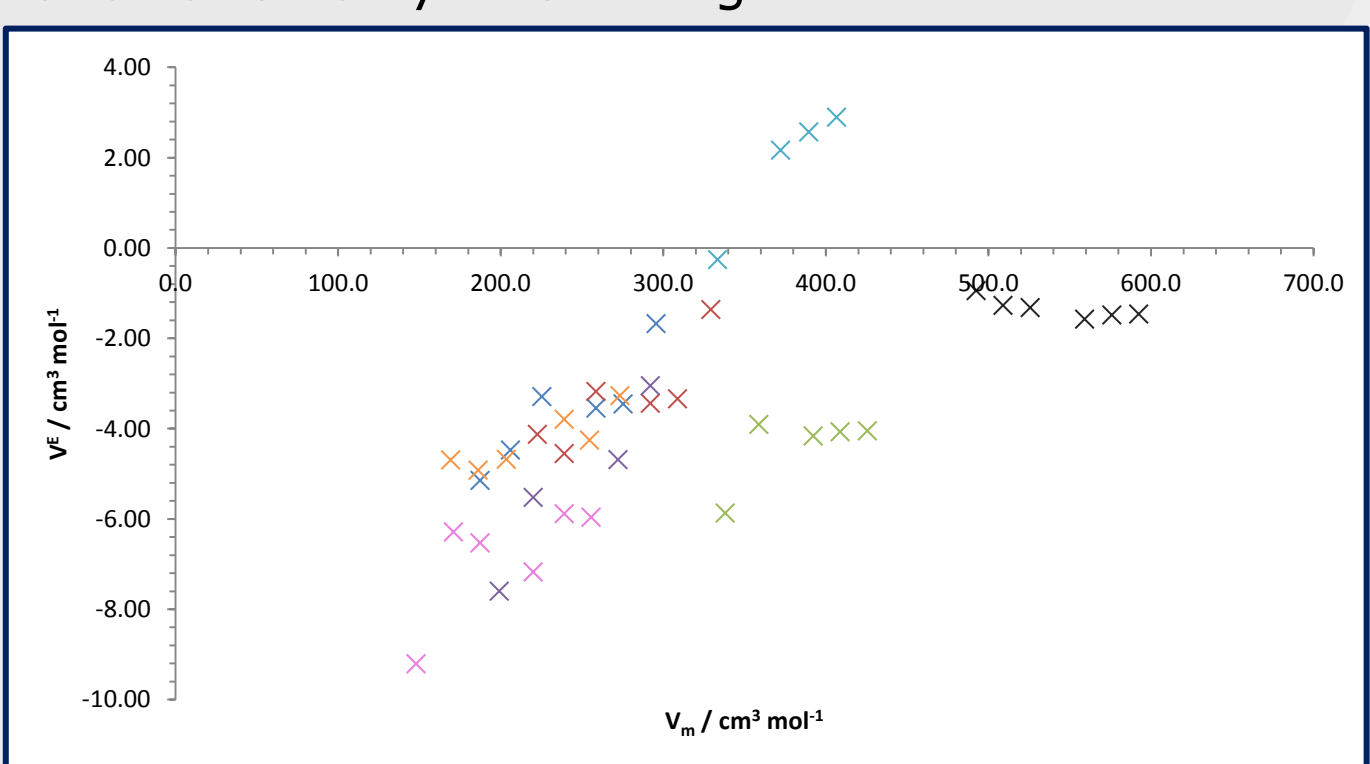
Graph 5: strong negative correlation between π^* and V^E , showing relation between the dipole moment and anion-cation interactions.



Graph 2: Refractive index is proportional to molar volume, deviations with non linear amines.



Graph 4: Refractive index increases with anion and cation alkyl chain length.



Graph 6: V^E decreases with increasing alkyl chain length, affected by hydrophobic effect.



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References

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Materials and Methods

- PIL Synthesis*: Each protic ionic liquid was prepared as previously described by Walker^[4].
- Karl-Fisher Titration*: Water content was measured for each of the PILs using a KEM Karl-Fisher Moisture Titrator MKS-500. Samples were only used if water was found to be below our limits of detection (<100ppm).
- Density*: All liquid density measurements were measured in triplicate using an Anton Parr DSA 5000 at 298K.
- Viscosity*: Dynamic viscosity measurements were recorded in triplicate with an AND SV-10 Vibro Viscometer at 298K.
- Refractive Index*: The refractive index at $\lambda = 589.3\text{nm}$ for each sample was measured in triplicate using a Mettler Toledo Refracto 30PX at 293K.
- Solvatochromism*: The polarity of the PILs and their precursors (when possible) were studied using the visible absorption spectrum of *N,N*-diethylnitroaniline to calculate π^* as described by Taft *et al.*^[5]. The v_{max} for the peak of highest visible absorbance was recorded in duplicate using a Fisher Scientific Evolution 60S Spectrophotometer at 293K.



From left to right: DSA 5000, Evolution 60S Spectrophotometer, Refracto 30PX, Karl Fisher Moisture Titrator MKS-500 and SV-10 Vibro Viscometer

Data processing

Molar Volume: $V_m = \frac{m_r(i)}{\rho_i}$

Molar Refractivity: $MR = \frac{n_{PIL}^2 - 1}{n_{PIL}^2 + 2} \cdot \frac{m_r(PIL)}{\rho_{PIL}}$

Excess Molar Volume: $V^E = \frac{(0.5 \cdot m_r(A)) + (0.5 \cdot m_r(B))}{\rho_{PIL}} - \left(\frac{0.5 \cdot m_r(A)}{\rho_A} + \frac{0.5 \cdot m_r(B)}{\rho_B} \right)$

Solvatochromic Polarity: $\pi^* = 0.314 \cdot (27.52 - v_{\text{max}}(NN))$

Lorentz-Lorenz Mixing Rule: $\frac{n_{PIL}^2 - 1}{n_{PIL}^2 + 2} = \phi_a \frac{n_a^2 - 1}{n_a^2 + 2} + \phi_b \frac{n_b^2 - 1}{n_b^2 + 2}$

Volume Fraction: $\phi_i = \frac{x_i V_i}{\sum x_i V_i}$

Definitions

$m_r(i)$: Molecular weight of *i* / g mol⁻¹

ρ_i : Density of *i* / g cm⁻³

n_i : Refractive index of *i*

$v_{\text{max}}(NN)$: Frequency of maximum absorption of *N,N*-diethylnitroaniline

x_i : Mole fraction of *i*

Where *i* = a protic ionic liquid (PIL), an acid (A) or an amine (B)

Conclusions

- Refractive index, viscosity and π^* relate well to changes in anion and cation alkyl chain length.
- Excess molar volume and Lorentz-Lorenz^[6] mixing rules for refractive index hold well for PILs with linear alkyl groups, deviations relatable to changes in steric effects.
- Deviations from the bulk trends of the above properties can be interpreted as being due to specific molecular organisation.
- Relation of the precursor properties to the resulting PIL properties offers insight into the scope for tailoring a PIL by simple, structural changes.
- The ΔpK_a values of many of these PILs are very similar, highlighting that the localisation of the labile proton is not the only determining factor of PIL properties. Non-covalent interactions such as Van Der Waals forces and hydrophobicity are crucially important^[7].

Future Work

- In our future work, we plan to increase the range of materials to investigate the effects of functional groups, unsaturated bonds, multiple ionicity and sterically bulky groups.
- We would also like to expand our solvatochromic analysis of PILs with additional parameters such as α , β and E_T^N ^[8].
- Ultimately, our goal is to develop an effective prediction relationship between protic ionic liquids and their corresponding precursors.

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