New Method Based on the UNIFAC-VISCO Model for the Estimation of Ionic Liquids Viscosity Using Data Recommended by Mathematical Gnostics

*Nan Zhao[1], Ryan Oozeerally[2], Volkan Degirmenci[2], Zdeněk Wagner[3], Magdalena Bendová[3], Johan Jacquemin[1]**

[1]*School of Chemistry and Chemical Engineering, Queen's University Belfast, UK*

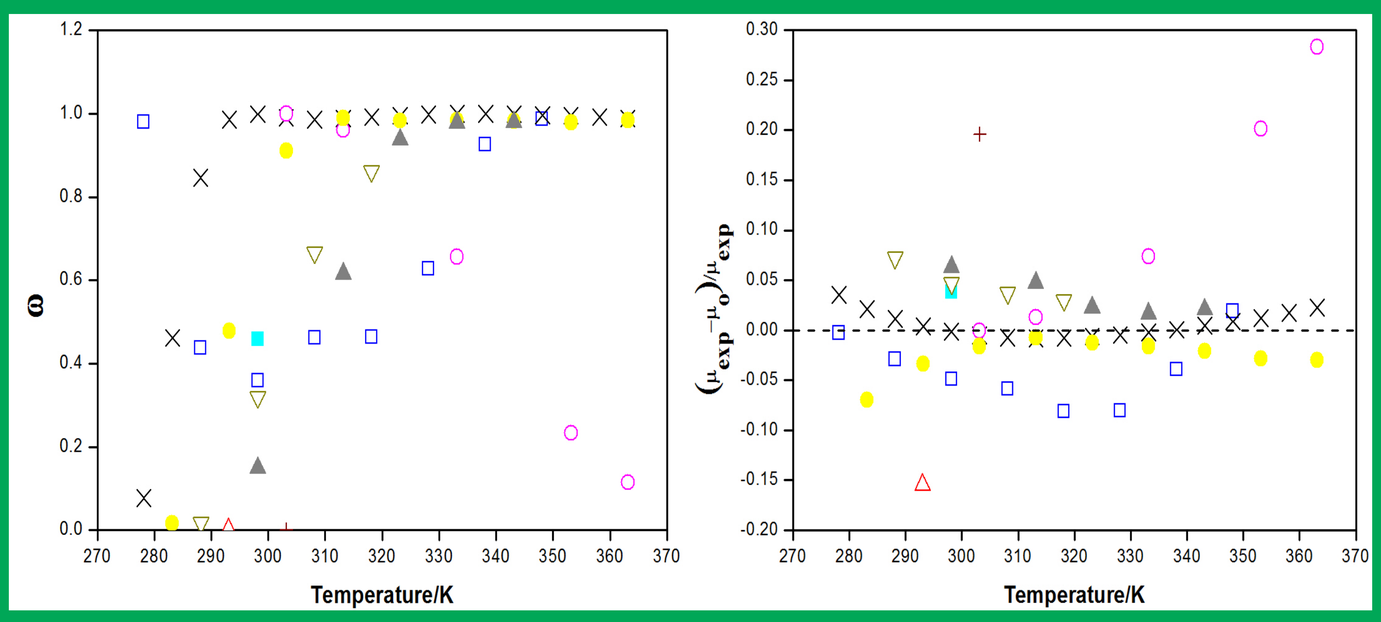
[2]*School of Engineering, University of Warwick, UK*

[3]*Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Czech Republic*

**Corresponding author: johan.jacquemin@qub.ac.uk*

Introduction

A modified UNIFAC-VISCO method was developed for correlation and estimation of viscosity of ILs as a function of temperature at 0.1 MPa using recommended data from the literature. During this work, experimental data were critically assessed using mathematical gnostics to highlight recommended data used then to establish the modified UNIFAC-VISCO group contribution model. Binary interaction parameters and ions Vogel-Fulcher-Tamman (VFT) parameters were determined by fitting the experimental viscosity and by minimizing the object function. Optimized parameters were used to predict the viscosity of pure and mixtures of ionic liquids with a good accuracy of 1.6% and 4.4%, respectively.



Data analysis by mathematical gnostics – $[C_2mim][OTf]$

Figure 1 shows the weight of experimental viscosity and figure 2 shows the comparison from the locations of the maximum distribution density: △, Abbott et al.;[1] ■, François et al.;[2] □, Rodríguez et al.;[3] ×, Freire et al.;[4] ○, Yusoff et al.;[5] ●, Seddon et al.;[6] +, Morgan et al.;[7] ▲, Tsamba et al.;[8] ▽, Vuksanovic et al.[9]

We recommend the dataset from Freire et al.[4] used for determination of binary interaction parameters.

Methodology

- The UNIFAC-VISCO model
  - A group contribution model
  - Used to predict the viscosities of organic liquid mixtures

$$\ln(\mu)=\sum_{i=1}^{C}x_i\ln(\mu_i\frac{V_i}{V_m})+\frac{g_c^E}{RT}-\frac{g_r^E}{RT}$$

- The modified UNIFAC-VISCO model for ionic liquids
  - Pure IL: **Ionic Liquid = [Cation]⁺ + [Anion]⁻** → **Component 1**, **Component 2**
  - Binary mixtures of ILs:

Ionic Liquid 1 + Ionic Liquid 2 → **Component 1**, **Component 2**

- **([Cation][Anion1] + [Cation][Anion2])**
- **([Cation1][Anion] + [Cation2][Anion])**
- **([Cation1][Anion1] + [Cation2][Anion2])**

- Parameters required in UNIFAC-VISCO model
  - Effective molar volume of cation/anion

$$V_{ion}(T^*)=\sum_{i=0}^{2}(a_i\cdot(T^*)^i),(T^*=T-298.15)$$

  - Volume R and surface area Q of ions – COSMO*therm*X
  - Effective viscosity of cation/anion – VFT behavior

$$\mu_{ion}=A\cdot\exp[\frac{B}{T-T_0}]$$

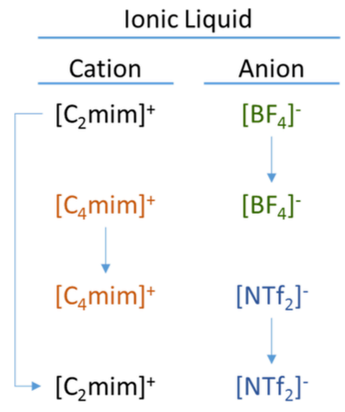
  - Binary interaction parameters α_{mn}

Methodology

- Marquardt optimization technique – *MATLAB*

$$Objective-Function=\frac{1}{M}\sum_{i=1}^{M}(\frac{\mu_{exp}-\mu_{cal}}{\mu_{exp}})^2\rightarrow\min$$

- Scheme to reduce the no. of parameters



Results and Conclusion

- Binary interaction parameters and ions VFT parameters for 70 pure ILs and eleven binary mixtures were optimized using 819 pure ILs and 966 binary mixtures experimental data, respectively.
- The correlation for pure ILs using the UNIFAC-VISCO method shows a good accuracy of 1.6%.
- The prediction for binary mixtures of ILs is highlighted by RAAD, lower than 4.4%.

Reference

1. Abbott et al. *Phys. Chem. Chem. Phys.* **2006**, 8, 4265-4279. 2. François et al. *Anal. Chim. Acta.* **2006**, 562, 164-170. 3. Rodríguez et al. *J. Chem. Eng. Data* **2006**, 2145-2155. 4. Freire et al *J. Chem. Eng. Data* **2011**, 56, 4813-4822. 5. Yusoff et al. *J. Chem. Eng. Data* **2013**, 58, 240-247. 6. Seddon et al. ACS Symposium Series; Washington, USA, 2002, Vol. 819, 34-49. 7. Morgan et al. *Ind. Eng. Chem. Res.* **2005**, 44, 4815-4823. 8. Tsamba et al. *J. Chem. Eng. Data* **2014**, 59, 1747-1754. 9. Vuksanovic et al. *Fluid Phase Equilib.* **2013**, 352, 100-109.