Predictive models for γ∞

Project Leader: Katarina Babić

Researcher(s): Boelo Schuur, Thomas Brouwer

E-mail: b.schuur@utwente.nl

Partners: AkzoNobel, DOW, DSM, SABIC, University of Twente

Budget: TKI-ISPT BL-20-05/07

Duration: 2014 - 2019

Objective:

Develop a general understanding of affinity scales based on molecular properties

Motivation:

The γ∞ is an important selection parameter for affinity separations. For i.a. prediction of extraction- and extractive distillation selectivities and potential azeotropes

Theoretical Framework

Several models from different backgrounds have been compared for their ability to predicts γ∞ of (a)polar solutes in (a)polar solvents.

Solvation Models (Hildebrand, Hansen, MOSCED)

In general, solvation models predict γ∞ by combining the Flory-Huggins size effect term and a calculation of the Flory-Huggins parameter, χ_{ij}.

$$ln\gamma_j = \underbrace{\chi_{ij}\phi_i^2}_{\text{“Like – dislike” term}} + \underbrace{\ln\left(\frac{\phi_j}{x_i}\right) + 1 - \frac{\phi_j}{x_i}}_{\text{Flory-Huggins size effect term}}$$

Where ϕ and x are resp. the volume and molar fraction.

$$\begin{cases} Hildebrand: \chi_{ij} = \dfrac{V_j}{RT}\left({}^i\delta - {}^j\delta\right)^2 \\ Hansen: \chi_{ij} = \alpha\dfrac{V_j}{RT}\left(\left({}^i\delta_D - {}^j\delta_D\right)^2 + 0{,}25\left({}^i\delta_P - {}^j\delta_P\right)^2 + \left({}^i\delta_H - {}^j\delta_H\right)^2\right) \\ MOSCED: \chi_{ij} = \dfrac{V_j}{RT}\left(\left({}^i\lambda - {}^j\lambda\right)^2 + \dfrac{q_1 q_2\left({}^i\tau - {}^j\tau\right)^2}{\psi_i} + \dfrac{\left({}^i\alpha - {}^j\alpha\right)\left({}^i\beta - {}^j\beta\right)}{\xi_i}\right) \end{cases}$$

For a more detailed explanation concerning individual parameters see (Hansen (2002), Barton (1991)).

Linear Solvation Energy Relationship (Abraham's model)

A linear relation between solute and solvent descriptors originates solvatochromic parameters and was adapted by Abraham for (non-)ionic species.

$$\begin{cases} MS: \log(P) = c + e\boldsymbol{E} + s\boldsymbol{S} + a\boldsymbol{A} + b\boldsymbol{B} + v\boldsymbol{V} \\ IL: \log(P) = (c_a + c_c) + (e_a + e_c)\boldsymbol{E} + (s_a + s_c)\boldsymbol{S} + \\ (a_a + a_c)\boldsymbol{A} + (b_a + b_c)\boldsymbol{B} + (v_a + v_c)\boldsymbol{V} \end{cases}$$

$$\log(\gamma^{\infty}) = \log\left(\frac{RT}{P^o_{solute}V_{m,solvent}}\right) - \log(P)$$

For a more detailed explanation concerning individual Abrahams parameters see Abraham (1999) & Jalan (2010).

Group Contribution Methods (UNIFAC, mod. UNIFAC (Do))

The most successful group contribution method was formulated by Fredenslund (1975) and later modified by Weidlich (1987) and Larsen (1987).

$$\ln\gamma_i^C = \ln\gamma_i^C + \ln\gamma_i^R$$

- Combinatorial term

$$\begin{cases} UNIFAC\ and\ mod.UNIFAC\ (Do): \ln\gamma_i^C = 1 - \phi_i{}' + \ln\phi_i{}' - 5\left(\sum_{k=1}^{n}\nu_k Q_k\right)\left(1 - \dfrac{\phi_i}{\theta_i} + \ln\dfrac{\phi_i}{\theta_i}\right) \\ mod.UNIFAC\ (Ly): \ln\gamma_i^C = 1 - \phi_i{}' + \ln\phi_i{}' \end{cases}$$

$$where\ \phi_i = \frac{\sum_{k=1}^{n}\nu_k R_k}{\sum_{j=1}^{n}\left(x_j\sum_{k=1}^{n}\nu_k R_k\right)},\ \phi_i' = \frac{\left(\sum_{k=1}^{n}\nu_k R_k\right)^a}{\sum_{j=1}^{n}\left(x_j\left(\sum_{k=1}^{n}\nu_k R_k\right)^a\right)}\ and\ \theta_i = \frac{\sum_{k=1}^{n}\nu_k Q_k}{\sum_{j=1}^{n}\left(x_j\sum_{k=1}^{n}\nu_k Q_k\right)}$$

Where Q_k, R_k and ν_k are resp. the group surface and volume contributions and the number of occurrences of that group. The a-parameter is 1 for UNIFAC, 0,67 for mod. UNIFAC (Ly) and 0,75 for the mod. UNIFAC (Do).

- Residual term;

$$\ln\gamma_i^R = \sum_k \upsilon_k^i\left(\ln\Gamma_k - \ln\Gamma_k^i\right)$$

Where Γ_k and Γ_k^i are resp. the activity of the group in a mixture and in the pure state.

For a more detailed explanation concerning UNIFAC parameters see Fredenslund (1975) , Larsen (1987) & Weidlich (1987).

Conductor like Screening Model for Real Solvents (COSMO-RS)

COSMO-RS uses quantum mechanical calculations to profile the charge density, or σ, of a molecule and statistical thermodynamics to predict molecular properties, such as γ∞.

$$E_{misfit}(\sigma,\sigma') = a_{eff}\frac{\alpha'}{2}(\sigma + \sigma')^2$$

$$E_{hb}(\sigma,\sigma') = a_{eff}c_{hb}\min((0,\min(0,\sigma_{done} + \sigma_{hb})\max(0,\sigma_{acc} - \sigma_{hb}))$$

$$E_{VdW}^X = \sum_{a\,\in\,X} a_\alpha\tau\left(e(\alpha)\right)$$

Where hydrogen bonding (HB) is assumed to occur in two segments;
HB-acceptor at σ_{hb} > 0,0085 e/Å² and HB-donor at σ_{hb} < -0,0085 e/Å².

For a more detailed explanation concerning COSMO-RS, see Klamt (2005).

Results:

Molecular Solvents

Training set
γ∞ Database[1] of: 527 molecular solvents (ranging from aliphatics to highly polar oxygenates)

Model comparison

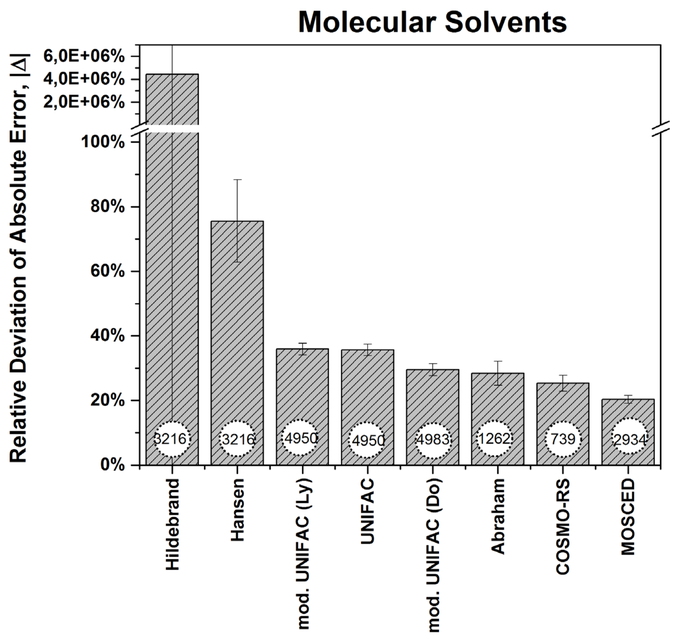

Figure 1: The relative deviation of the absolute error (|Δ|) between predicted and measured γ∞ of solutes at 298.15°C in molecular solvents of 8 models. Within the dotted circles the amount of individual correlations made is shown for each model. A confidence interval of 95% is shown.

Ionic Liquids

Training set
γ∞ Database[1] of: 252 Ionic Liquids

Model comparison

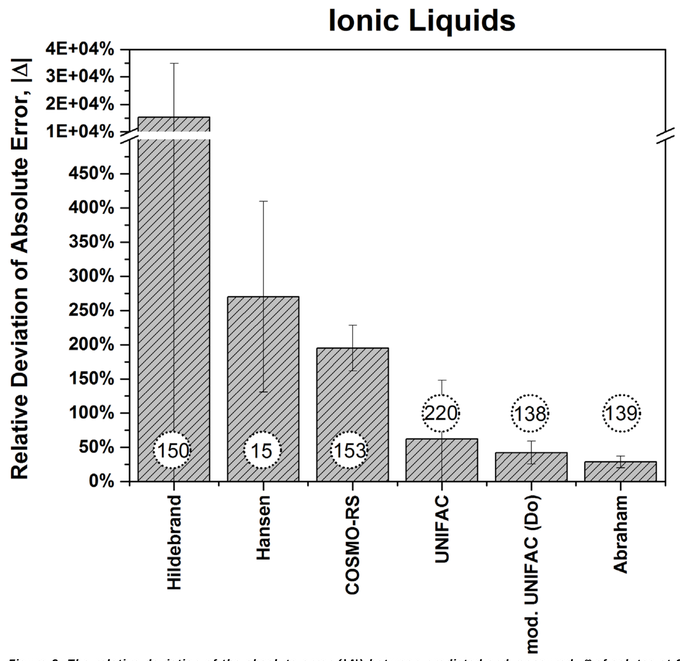

Figure 2: The relative deviation of the absolute error (|Δ|) between predicted and measured γ∞ of solutes at 298.15°C in ionic liquids of 6 models. Within the dotted circles the amount of individual correlations made is shown for each model. A confidence interval of 95% is shown.

Conclusion:

- The additional ionic interactions within ionic liquids complicates an accurate prediction of γ∞ for many models.
- One-parameter models e.g. Hildebrand, break down due to its insufficiently to account for hydrogen bonding effects.
- Increasing the amount of parameters to three (Hansen) or four (MOSCED) significantly increases the prediction of γ∞ due to the description of the hydrogen bonding effects. MOSCED is superior due to its ability to distinguishes the hydrogen bonding donation and accepting effects.
- Group Contribution methods (UNIFAC, mod. UNIFACC (Ly) and mod. UNIFAC (Do)) perform with an accuracy comparable to COSMO-RS, though the versatility of COSMO-RS should be mentioned for it is a purely theoretical model. Note that the mod. UNIFAC (Do) and UNIFAC makes superior predictions for Ionic Liquids than COSMO-RS.
- Overall, the MOSCED and Abrahams model resp. predict most accurately the γ∞ of molecular solvents and ionic liquids, though the large amount of parameters required could be a drawback and may limit applicability.

References:

[1] An extensive database was gathered by importing γ∞ data from 857 research papers.

Hansen (2002) - Hansen, Charles M. Hansen solubility parameters: a user's handbook. CRC press, 2002.
Barton (1991) - Barton, Allan FM. CRC handbook of solubility parameters and other cohesion parameters. CRC press, 1991.
Abraham (1999) - Abraham, Michael H., Colin F. Poole, and Salwa K. Poole. "Classification of stationary phases and other materials by gas chromatography." Journal of Chromatography A 842.1-2 (1999): 79-114.
Jalan (2010) - Jalan, Amrit, et al. "Predicting solvation energies for kinetic modeling." Annual Reports Section" C"(Physical Chemistry) 106 (2010): 211-258.
Fredenslund (1975) - Fredenslund, Aage, Russell L. Jones, and John M. Prausnitz. "Group-contribution estimation of activity coefficients in nonideal liquid mixtures." AIChE Journal 21.6 (1975): 1086-1099.
Weidlich (1987) - Weidlich, Ulrich, and Juergen Gmehling. "A modified UNIFAC model. 1. Prediction of VLE, hE, and. gamma.. infin." Industrial & engineering chemistry research 26.7 (1987): 1372-1381.
Klamt (2005) - Klamt, Andreas. COSMO-RS: from quantum chemistry to fluid phase thermodynamics and drug design. Elsevier, 2005.
Larsen, Bent L., Peter Rasmussen, and Aage Fredenslund. "A modified UNIFAC group-contribution model for prediction of phase equilibria and heats of mixing." Industrial & engineering chemistry research 26.11 (1987): 2274-2286.