FAKULTÄT V
INSTITUT FÜR REINE UND ANGEWANDTE CHEMIE

EXTRAPOLATION/INTERPOLATION OF INFINITE DILUTION ACTIVITY COEFFICIENT DATA BETWEEN SOLVENTS

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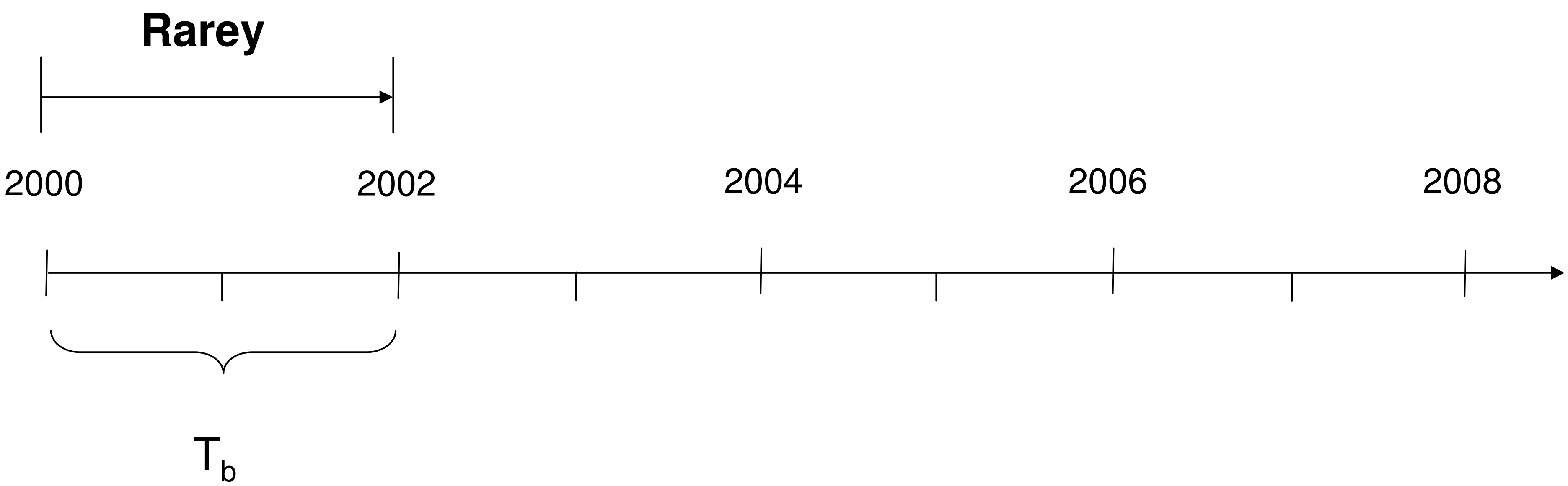
Overview

- Project Background
- Extrapolation in the Case of Alkane Solvents
- Applications
- Alcohol Interpolation between Alkanes and Water
- Further Work
- Acknowledgements

Project Background



W. Cordes, J. Rarey, *A New Method for the Estimation of the **Normal Boiling Point** of Non-Electrolyte Organic Compounds*, Fluid Phase Equilibria, 201/2, 397-421 (2002).

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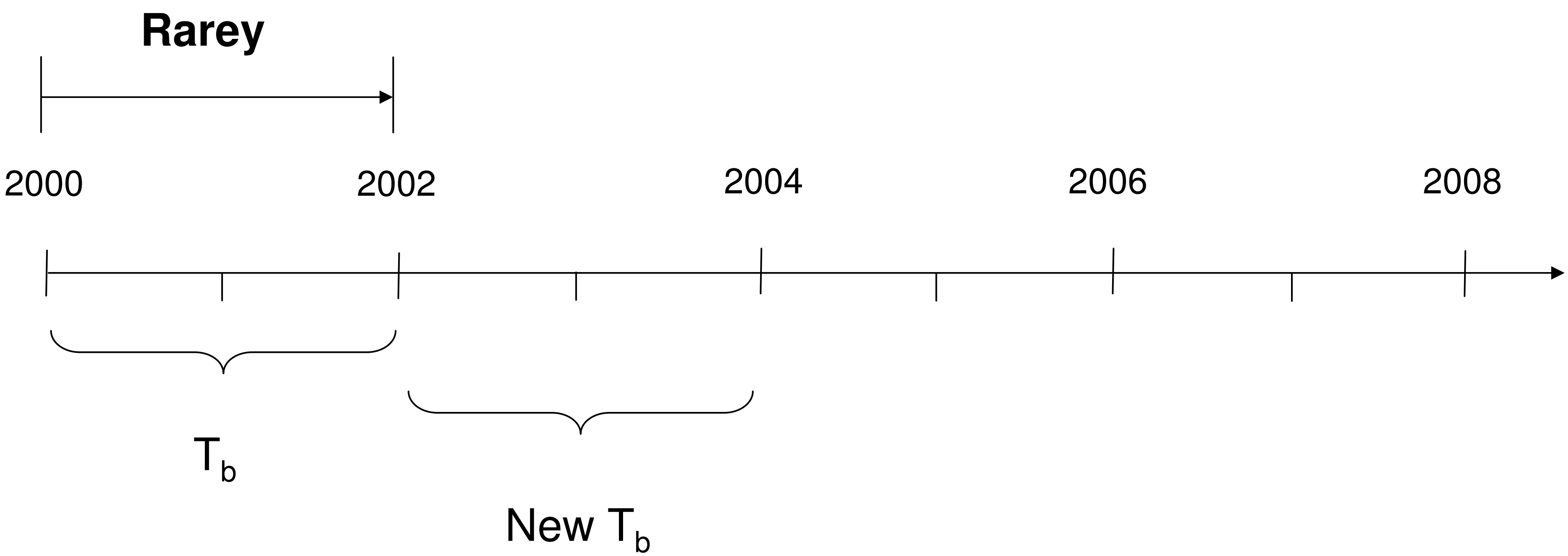

Y. Nannoolal, J. Rarey , D. Ramjugernath, W. Cordes, *Estimation of Pure Component Properties, Part 1: Estimation of the* ***Normal Boiling Point*** *of Non-Electrolyte Organic Compounds via Group Contributions and Group Interactions*, Fluid Phase Equilibria, 226, 45-63, 2005.

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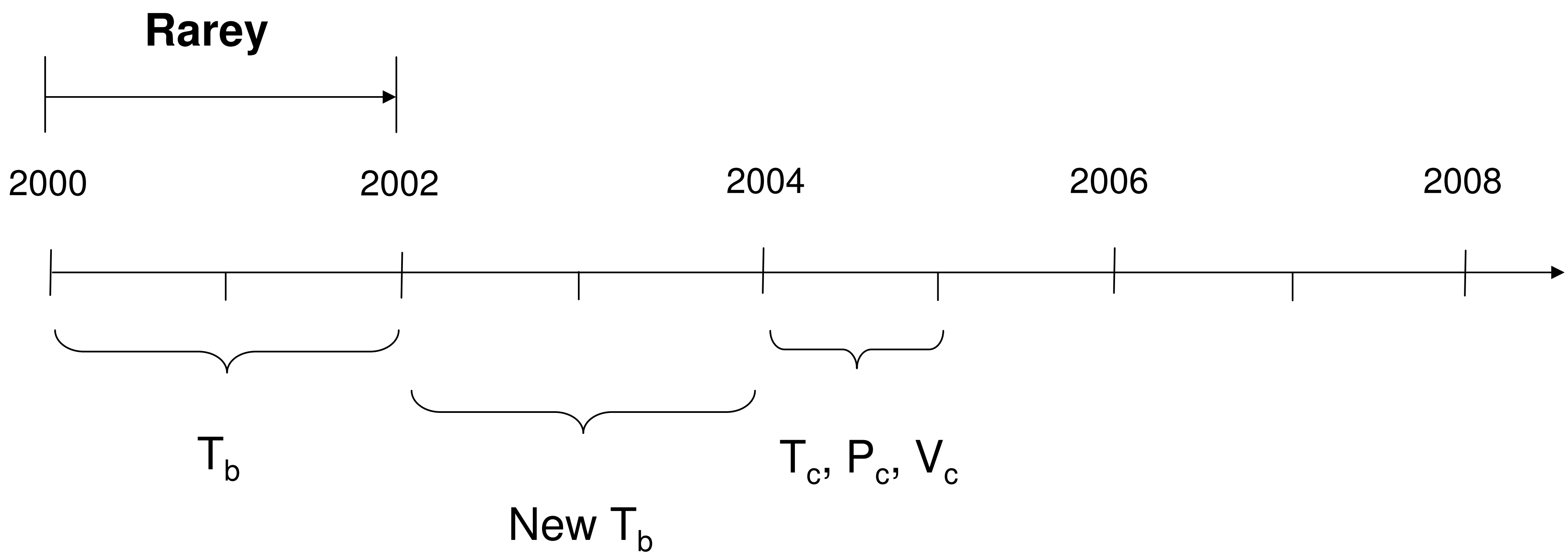
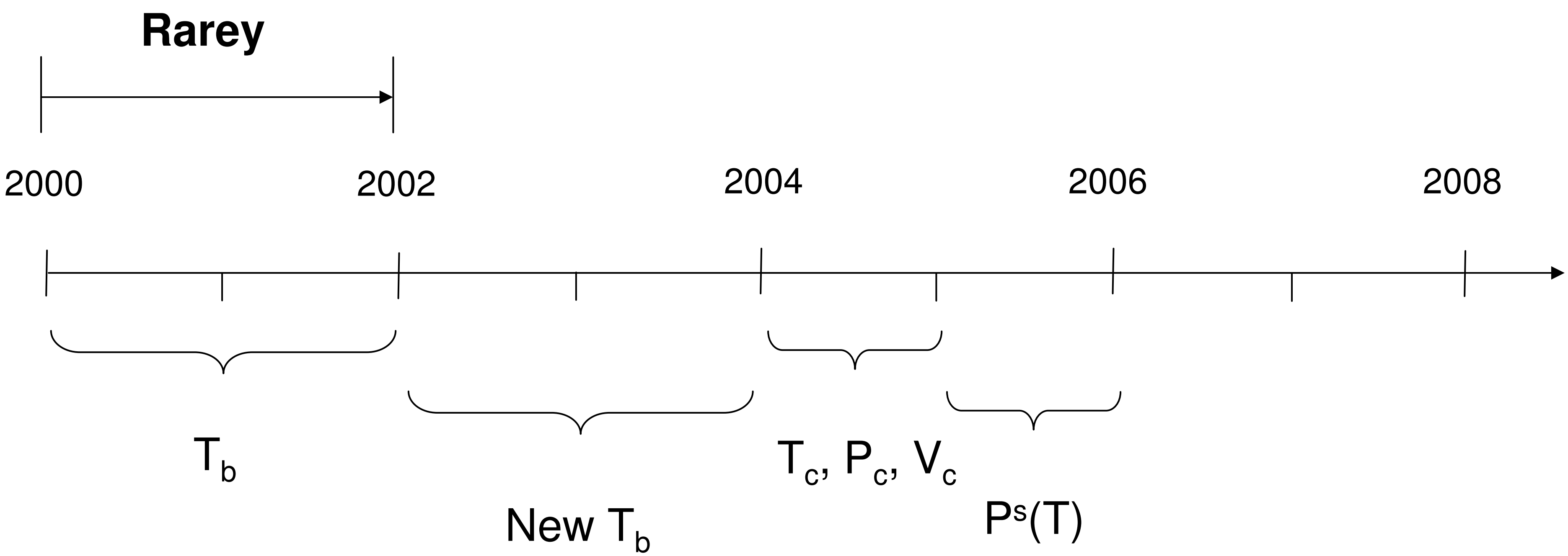


Nannoolal, Y., Rarey, J., Ramjugernath, D., Estimation of Pure Component Properties Part 2: Estimation of **Critical Data** by Group Contribution., *Fluid Phase Equilib.*, 252 (2007) 1.

Project Background



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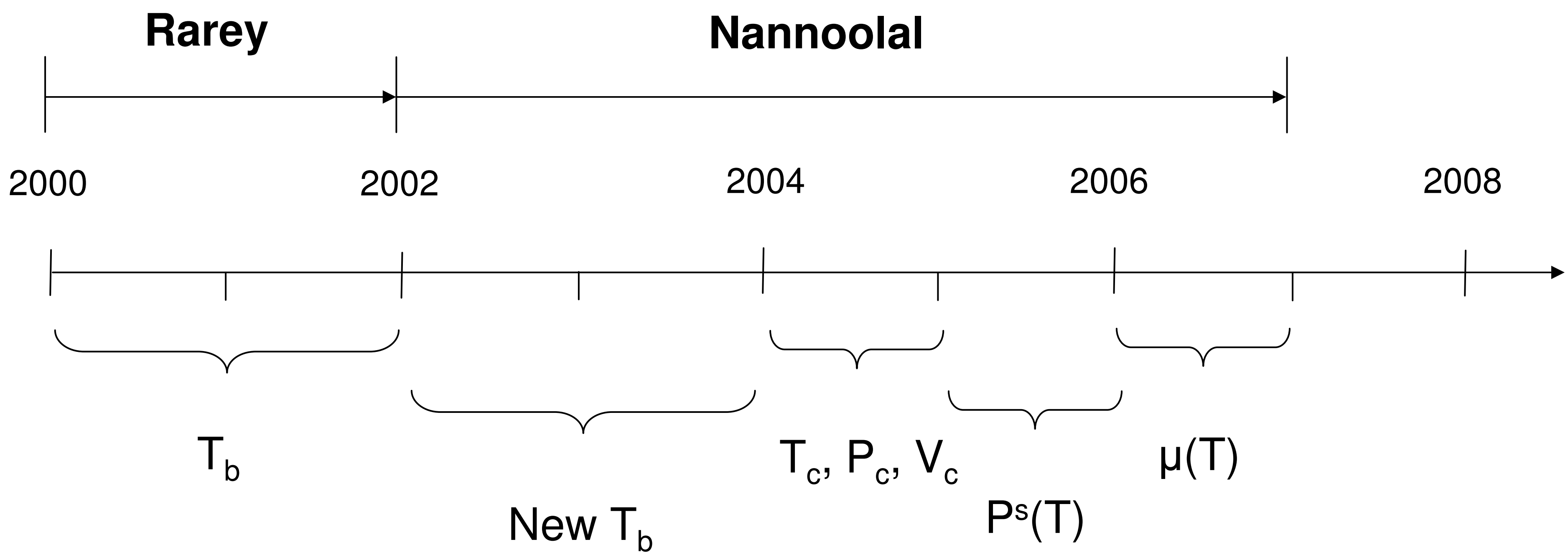
Project Background



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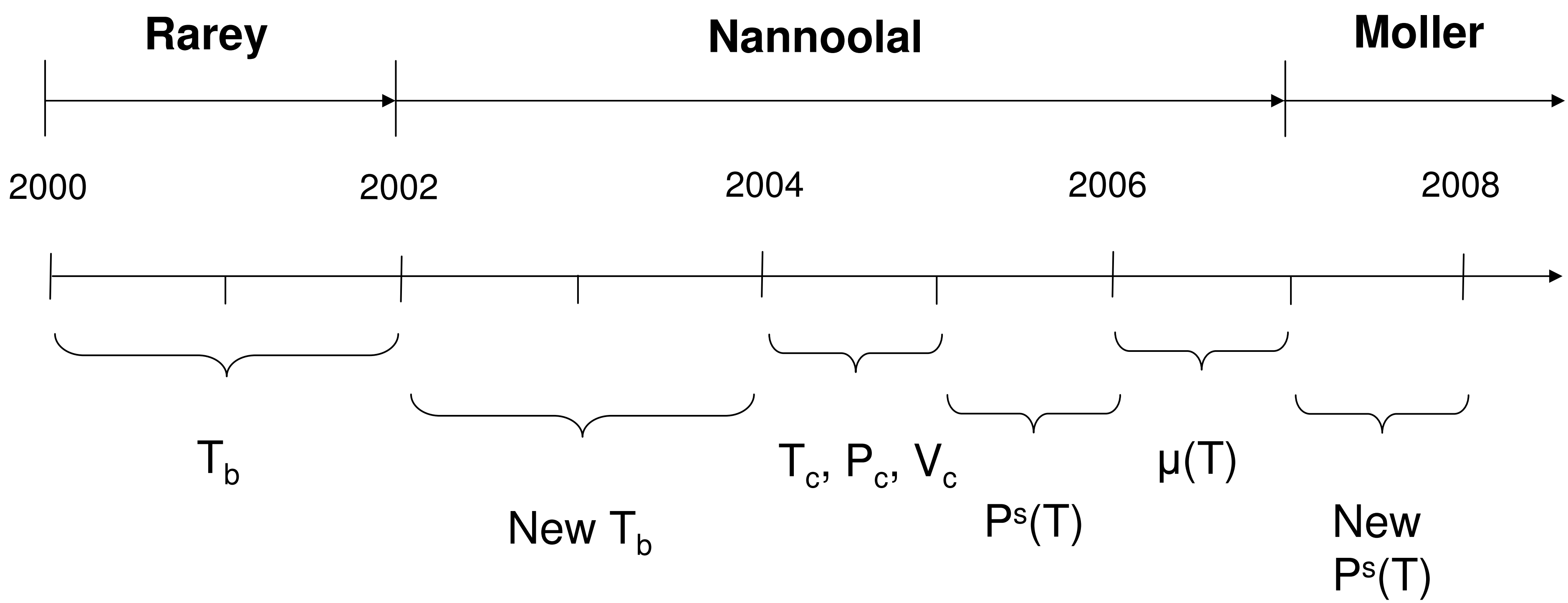
Project Background



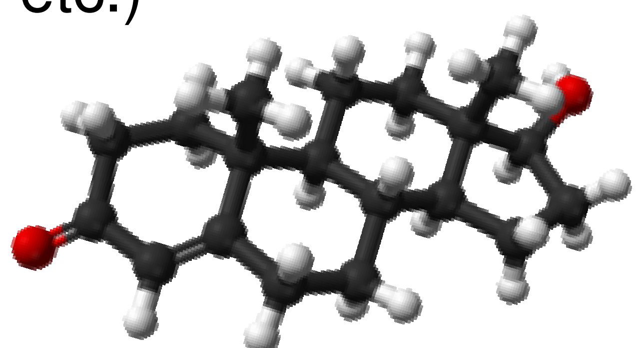
Moller, B., Rarey, J., Ramjugernath, D., Estimation of the **Vapour Pressure** of Non-Electrolyte Organic Compounds via Group Contributions and Group Interactions., *J. Mol. Liq.* 143 (2008) 52

Project Background

- Current work:

"Prediction of the activity of complex multifunctional organic compounds in common solvents"

- Useful for:
  - Design of separation equipment
  - Partitioning between compartments
  - …
- Current methods (UNIFAC, COSMO etc.)



Simplify the Problem

$$\gamma = f(x, T, P, solvent, solute)$$

- Solvent
  - Only reference solvents
- Concentration
  - Solid solubility data mainly of interest
  - Only at infinite dilution (x < 0.01)
- Pressure
  - Small at low to moderate pressures
- Temperature
  - Non-trivial
  - Only at 298 K

Available Data

- Most frequent solvents in the Dortmund Data Bank (γ^{∞} data)
  - Water
  - Others ???

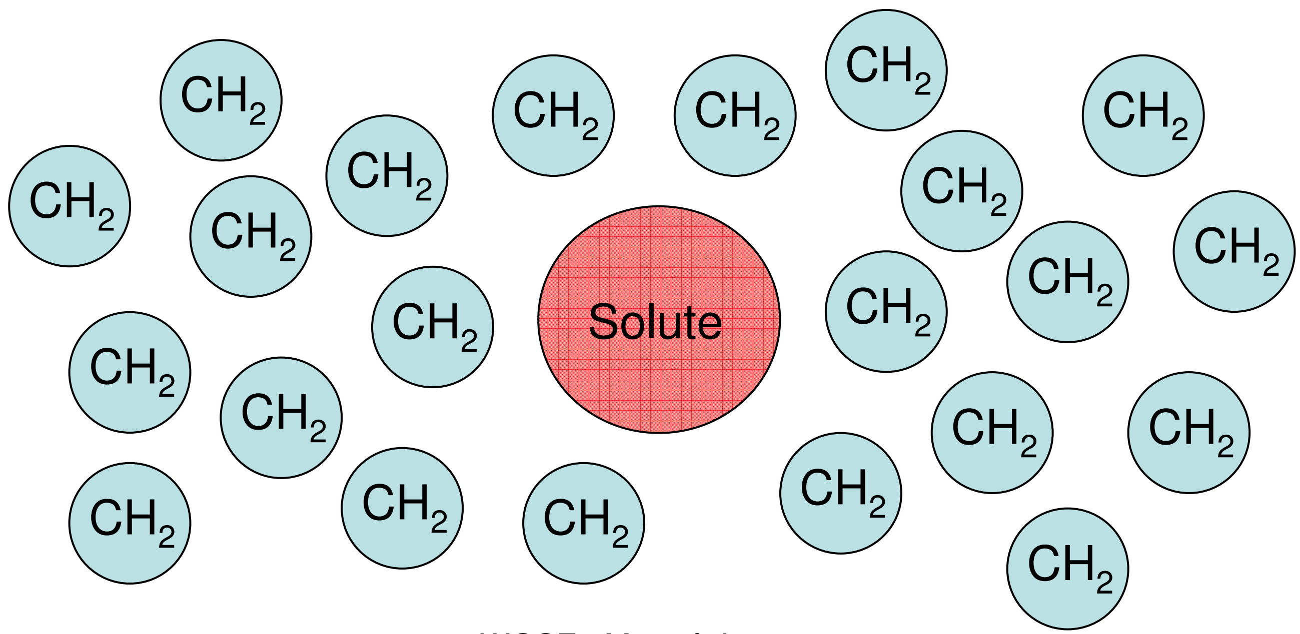
alkane
water

Solvent	No. Solutes
Water	585
Squalane	207
Hexadecane	198
Sulfolane	137
1-Octanol	128
Phthalic acid dinonyl ester	126
Heptane	116
N-Methyl-2-pyrrolidone	115
Octadecane	103
19,24-Dioctadecyldotetracontane	99

Reduction to a Common Solvent - Hexane

- Combinatorial and residual contribution
- Solution of groups concept:

"Residual contributions for a single solute in any alkane solvent **at infinite dilution** are identical"



Reduction to a Common Solvent - Hexane

- Expressing this mathematically:
- Activity coefficient made up of a combinatorial and residual contribution:

$$\gamma_{1,hexane}^{\infty} = \gamma_{1,hexane}^{R,\infty} \times \gamma_{1,hexane}^{C,\infty}$$

$$\gamma_{1,squalane}^{\infty} = \gamma_{1,squalane}^{R,\infty} \times \gamma_{1,squalane}^{C,\infty}$$

Reduction to a Common Solvent - Hexane

- Expressing this mathematically:
- Taking the ratio, the residuals cancel:

$$\frac{\gamma_{1,hexane}^{\infty}}{\gamma_{1,squalane}^{\infty}} = \frac{\gamma_{1,hexane}^{R,\infty} \times \gamma_{1,hexane}^{C,\infty}}{\gamma_{1,squalane}^{R,\infty} \times \gamma_{1,squalane}^{C,\infty}}$$

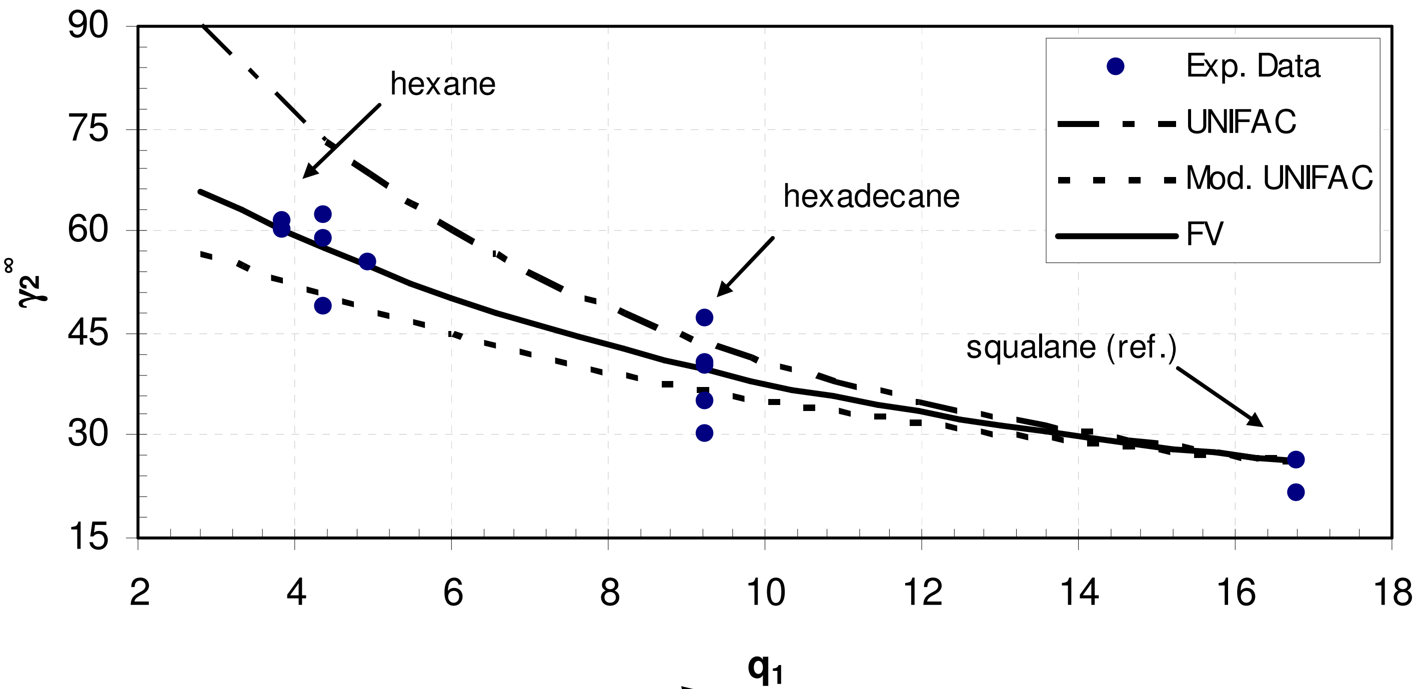
Reduction to a Common Solvent - Hexane

- Expressing this mathematically:
- In general form:

$$\gamma_{1,hexane}^{\infty} = \gamma_{1,reference}^{\infty} \frac{\gamma_{1,hexane}^{C,\infty}}{\gamma_{1,reference}^{C,\infty}}$$

Performance of Combinatorial Expressions

- Ethanol (2) in alkanes (1) …



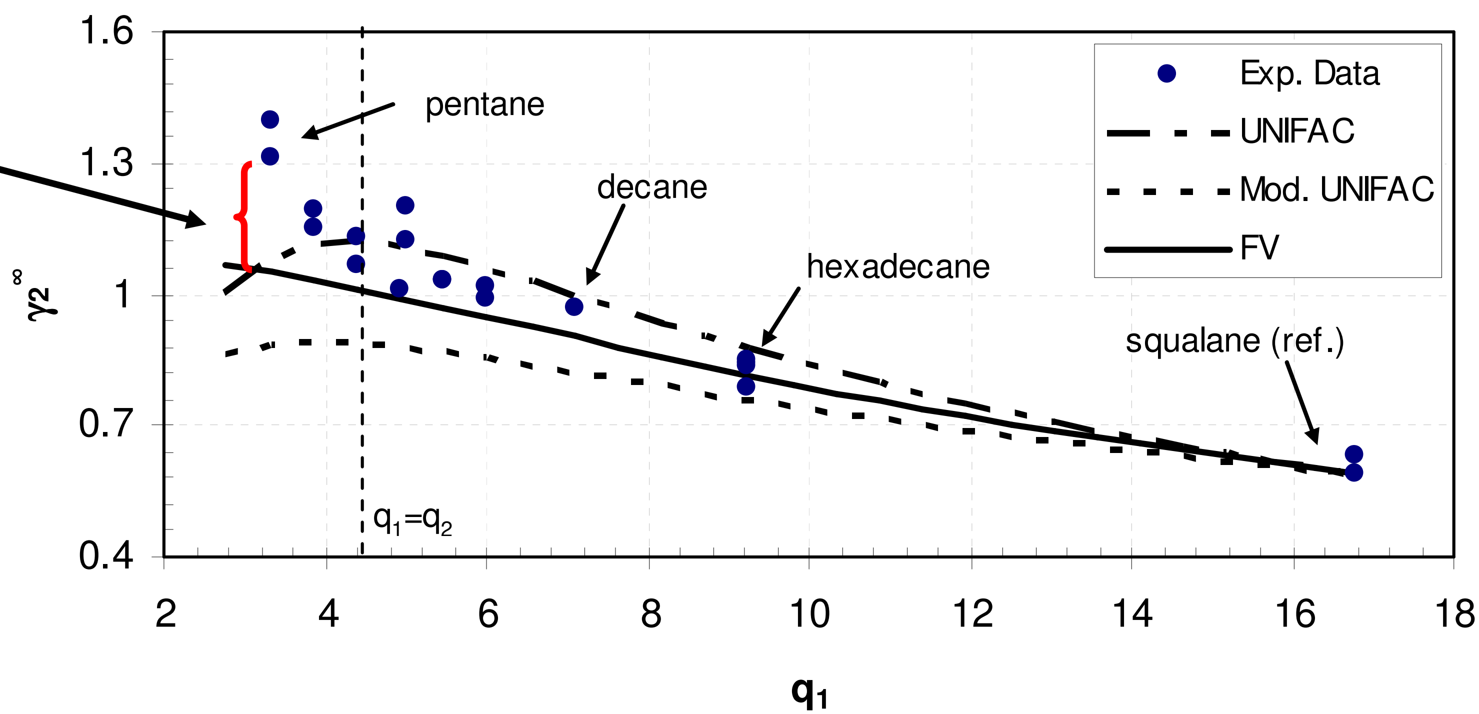
The UNIQUAC surface area for the alkane solvent

FV – Free Volume

Performance of Combinatorial Expressions

- Ethylcyclohexane (2) in alkanes (1) …

Error starts to become noticeable when $q_1/q_2 < 0.8$



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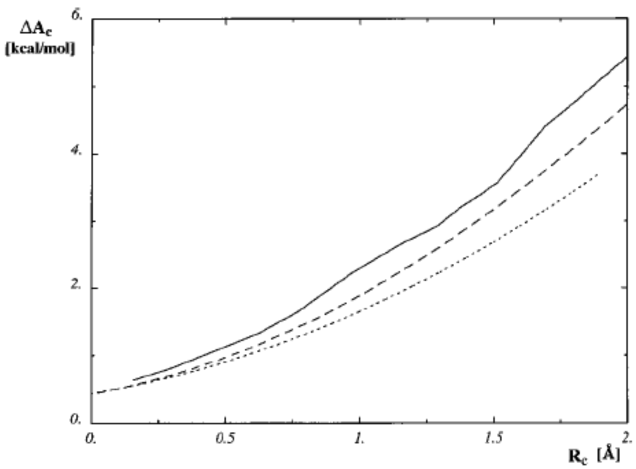
Performance of Combinatorial Expressions



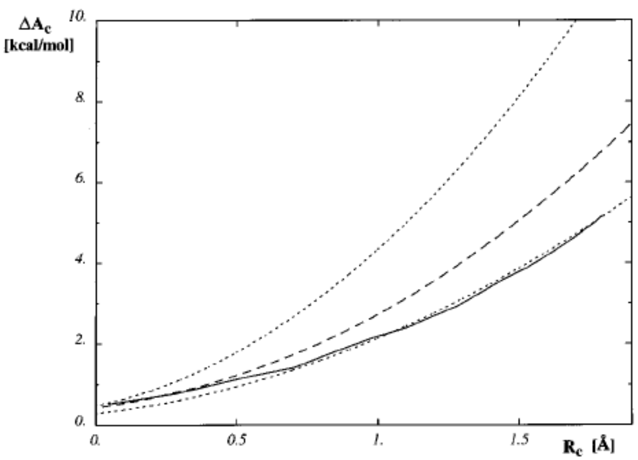


Figure 2. Comparison of the work of cavity formation ΔA_c computed with the two simulation methods RP (—) and TP (– – –) and with SP theory (- - -) as a function of the radius of the cavity R_c in hexane (a, top) and in water (b, bottom). In water, the upper and lower SP curves were computed with the σ (3.17 Å) and the most probable distance (2.8 Å), respectively.

Work of cavity formation as a function of cavity size from molecular simulation [1] in:

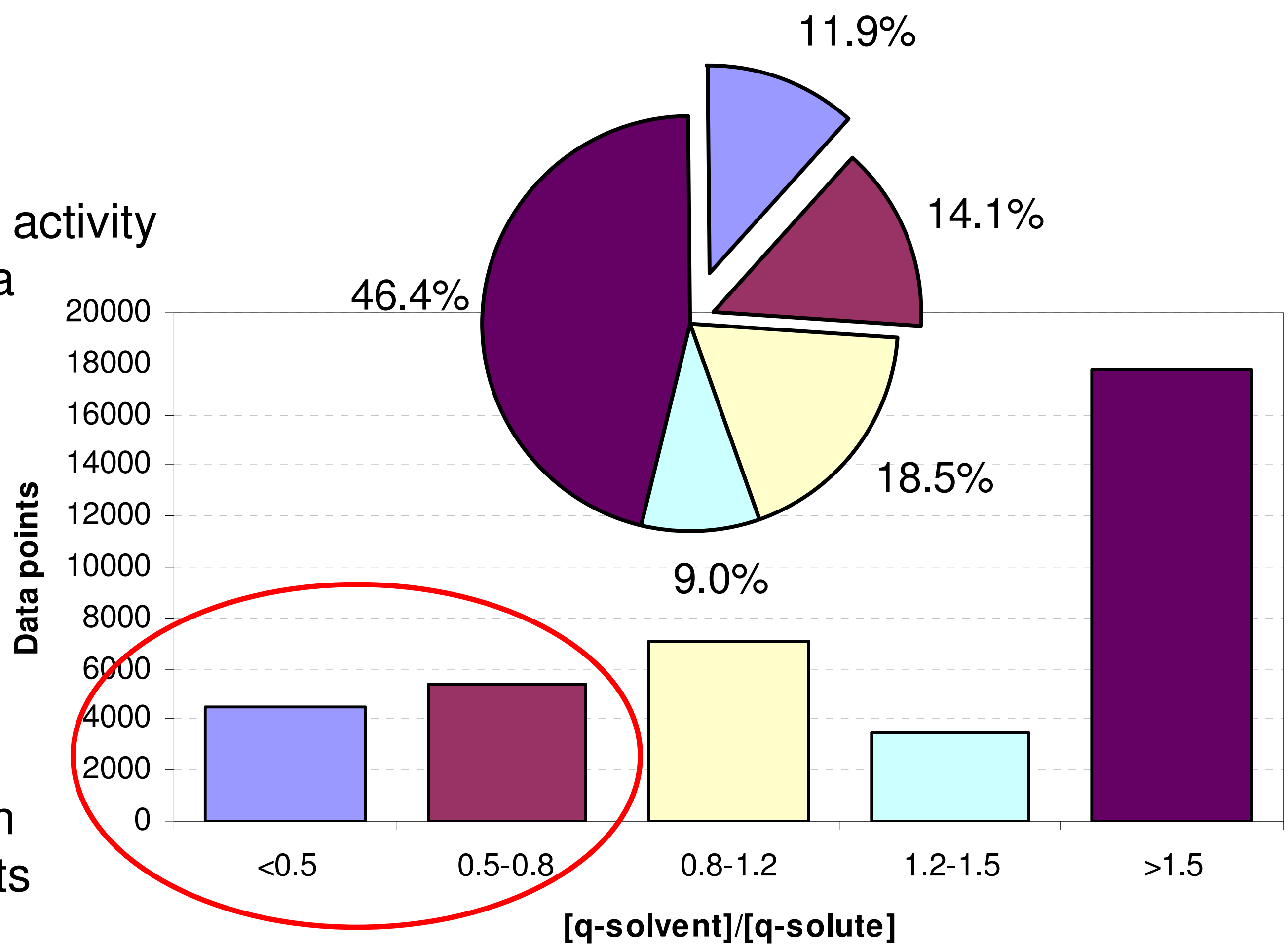
Hexane

Water

[1] Prevost et al., Free Energy of Cavity Formation in Liquid Water and Hexane. *J. Phys. Chem.* **1996,** *100,* 2738-2743

Performance of Combinatorial Expressions

Infinite dilution activity coefficient data



Big solutes in small solvents

New Combinatorial Expression

- Propose the following correction to the combinatorial:

$$\ln \gamma_2^{\text{C-Cav},\infty} = \ln \gamma_2^{\text{C},\infty} + \ln \gamma_2^{\text{Cav},\infty}$$

Free-Volume Expression

$$\ln \gamma_2^{\text{Cav},\infty} = \left(\frac{V_2^{FV}}{V_1^{FV}} - \frac{V'^{FV}_2}{V'^{FV}_1} \right)$$

$$V'^{FV}_i = \left(V_{m,i}\right)^{2/3} - \left(V_i^*\right)^{2/3}$$

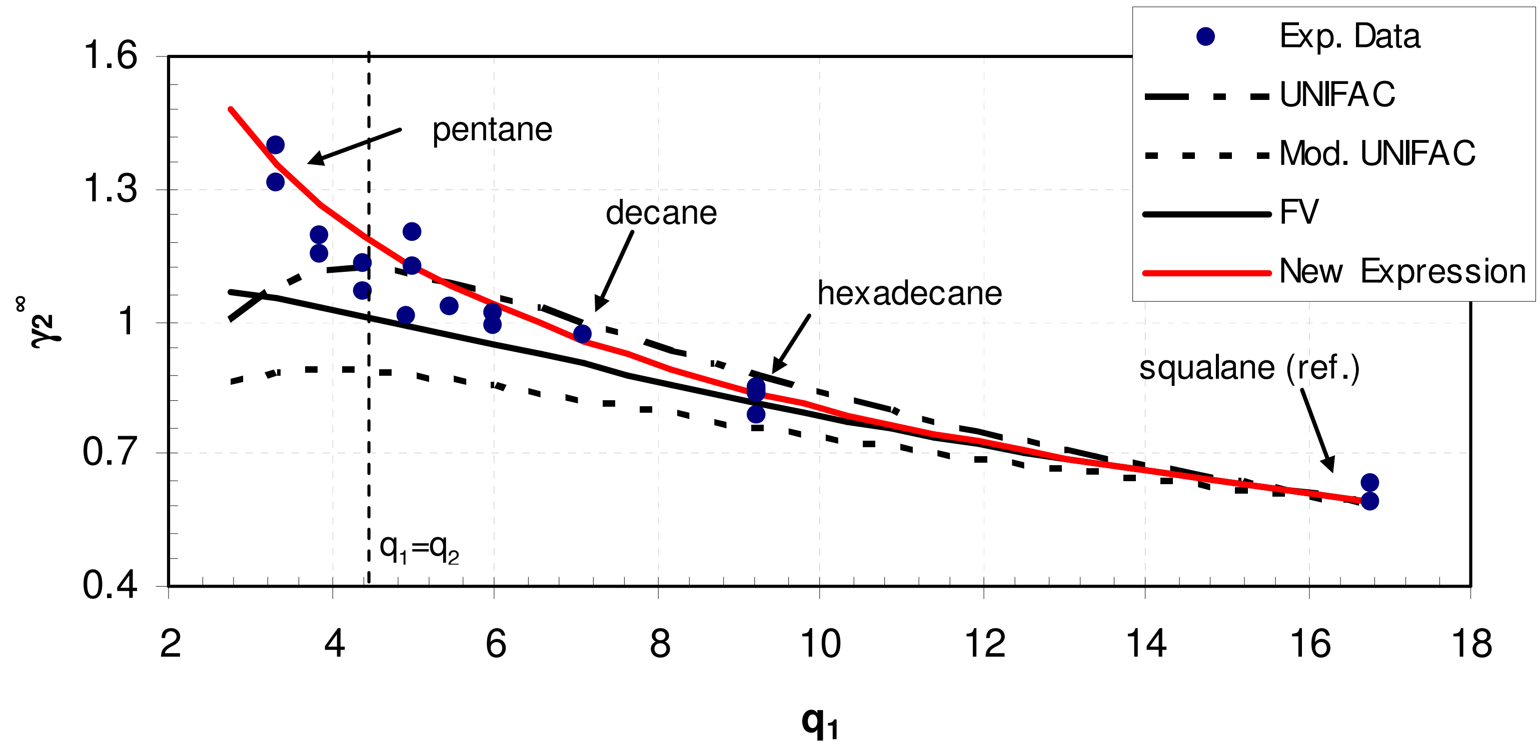
$$V_i^{FV} = V_{m,i} - V_i^*$$

$V_{m,i}$ - Liquid molar volume (cm^3/mol)

V_i^* - Van der Waals volume (cm^3/mol)

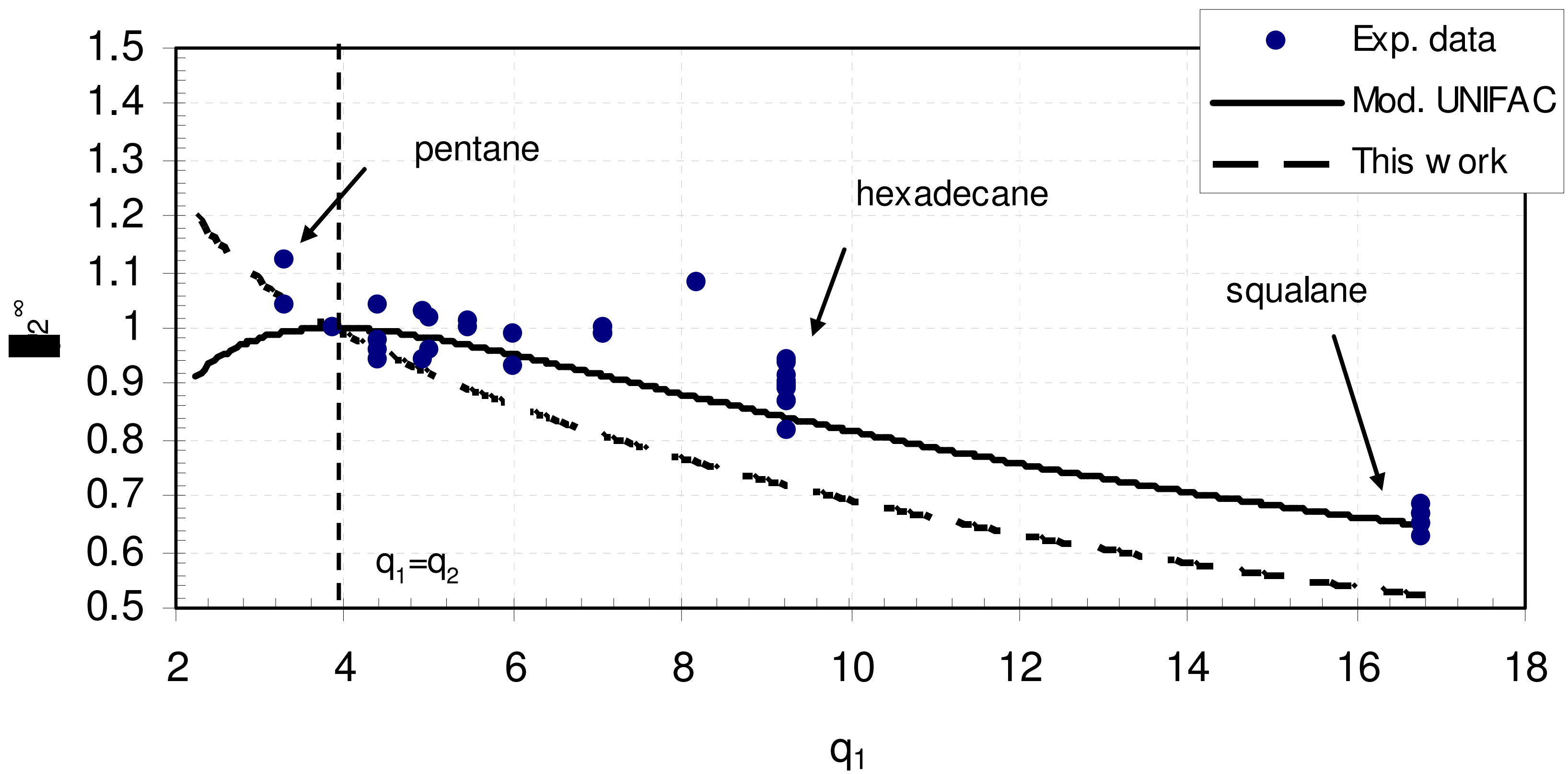
Performance of the New Combinatorial Expression

- Ethylcyclohexane (2) in alkanes (1) …



Performance of the New Combinatorial Expression

- Hexane (2) in alkanes (1) …



Performance of the New Combinatorial Expression

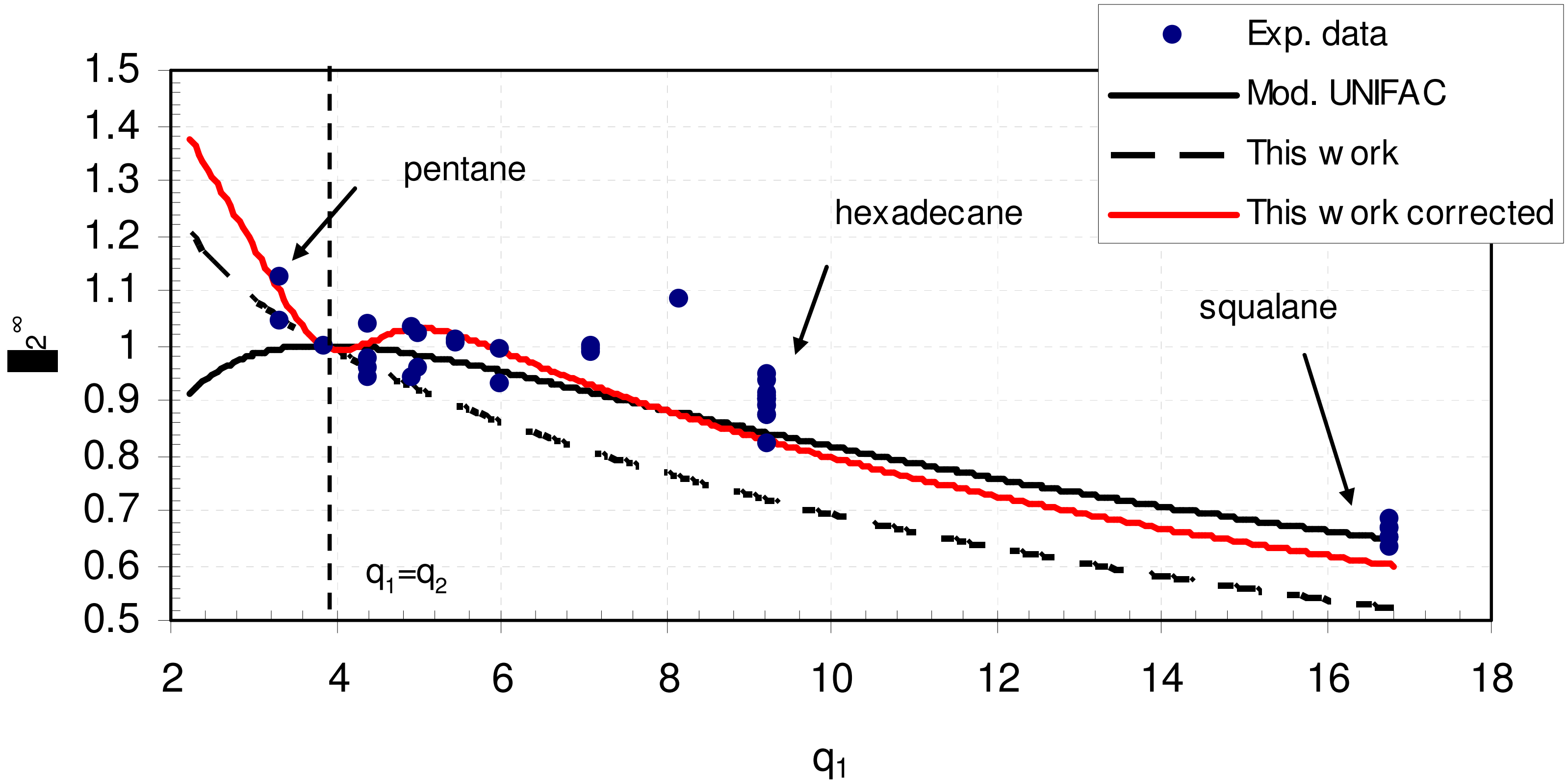
- Cavitation term empirically modified:

$$\gamma_2^{Cav,\infty}\Big|_{corrected} = \gamma_2^{Cav,\infty} \times \left(1.15 - 0.15 \times \exp\left(-0.5\left(q_1 - q_2\right)^2 - 0.5\left(r_1 - r_2\right)^2\right)\right)$$

- Step function allows an activity coefficient of 1 for pure component γ^∞

Performance of the New Combinatorial Expression

- Hexane (2) in alkanes (1) …



Performance of the New Combinatorial Expression

'Blindly' (no changing of the parameters, only swapping the combinatorial expressions) applying this combinatorial expression to original UNIFAC:

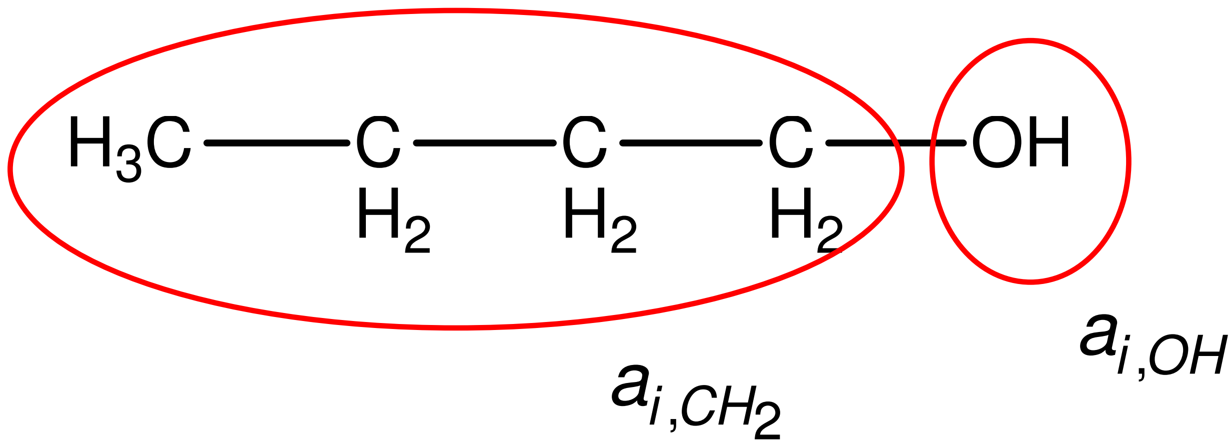
Combinatorial	Relative Mean Deviation (%) in $\ln\gamma^{\infty}$	Number of data points
Original	88.0	29344
This work	71.1	29336

Note: Only data for water were excluded due to the combinatorial expression in this work giving unrealistically large values.

Applications

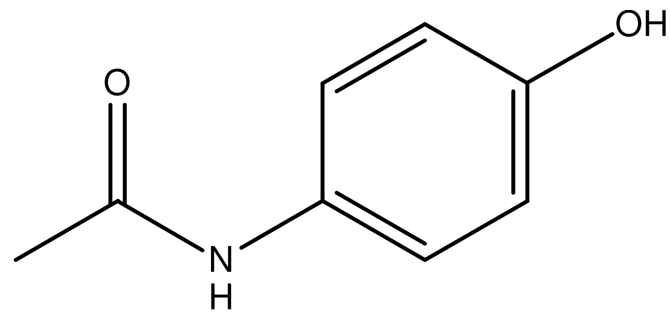
- Development of combinatorial expressions
- Measurements of high boilers in low(er) boilers are difficult …

Extension to Other Solvents - Alcohols



Extension to Other Solvents - Alcohols

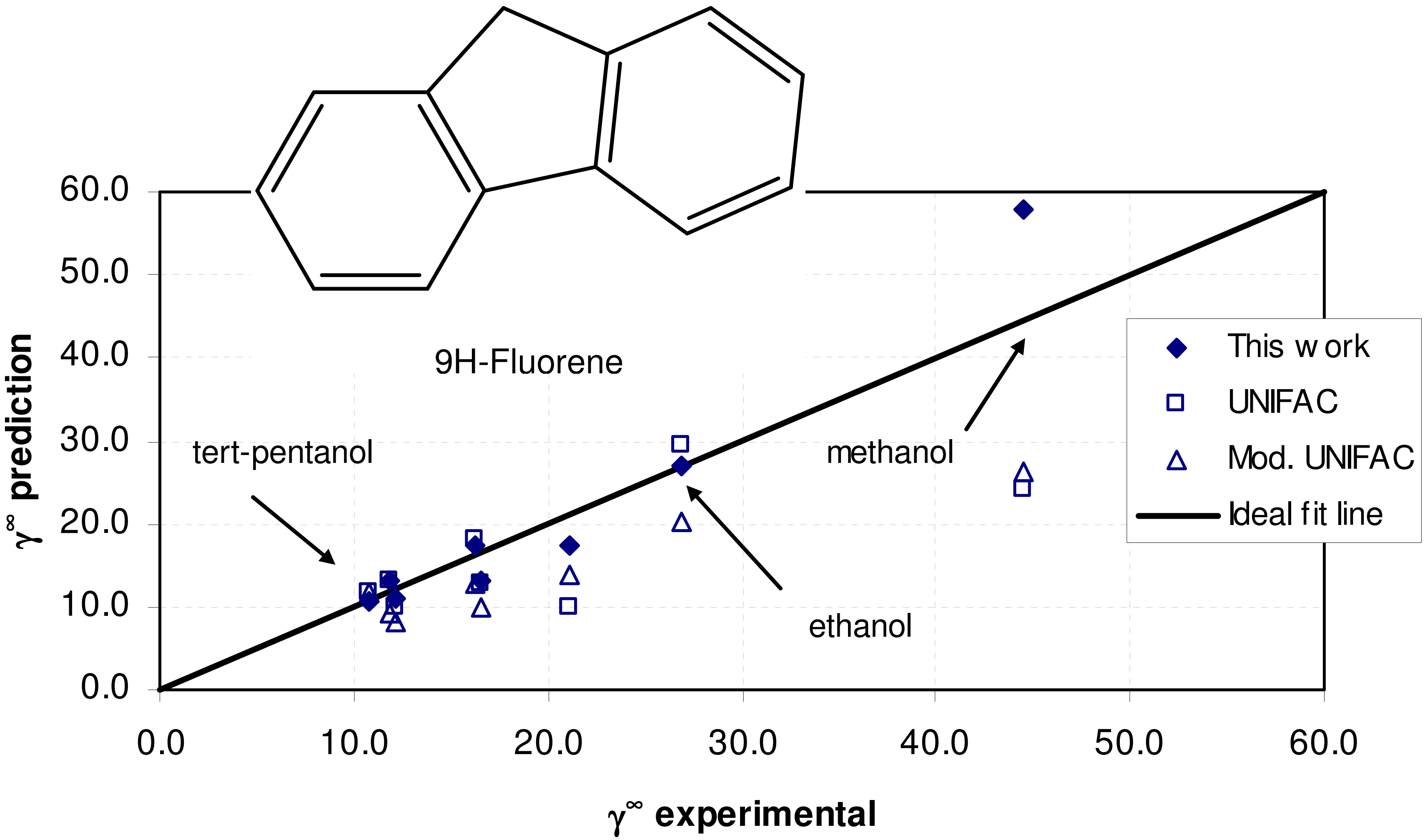
Solute



Paracetamol

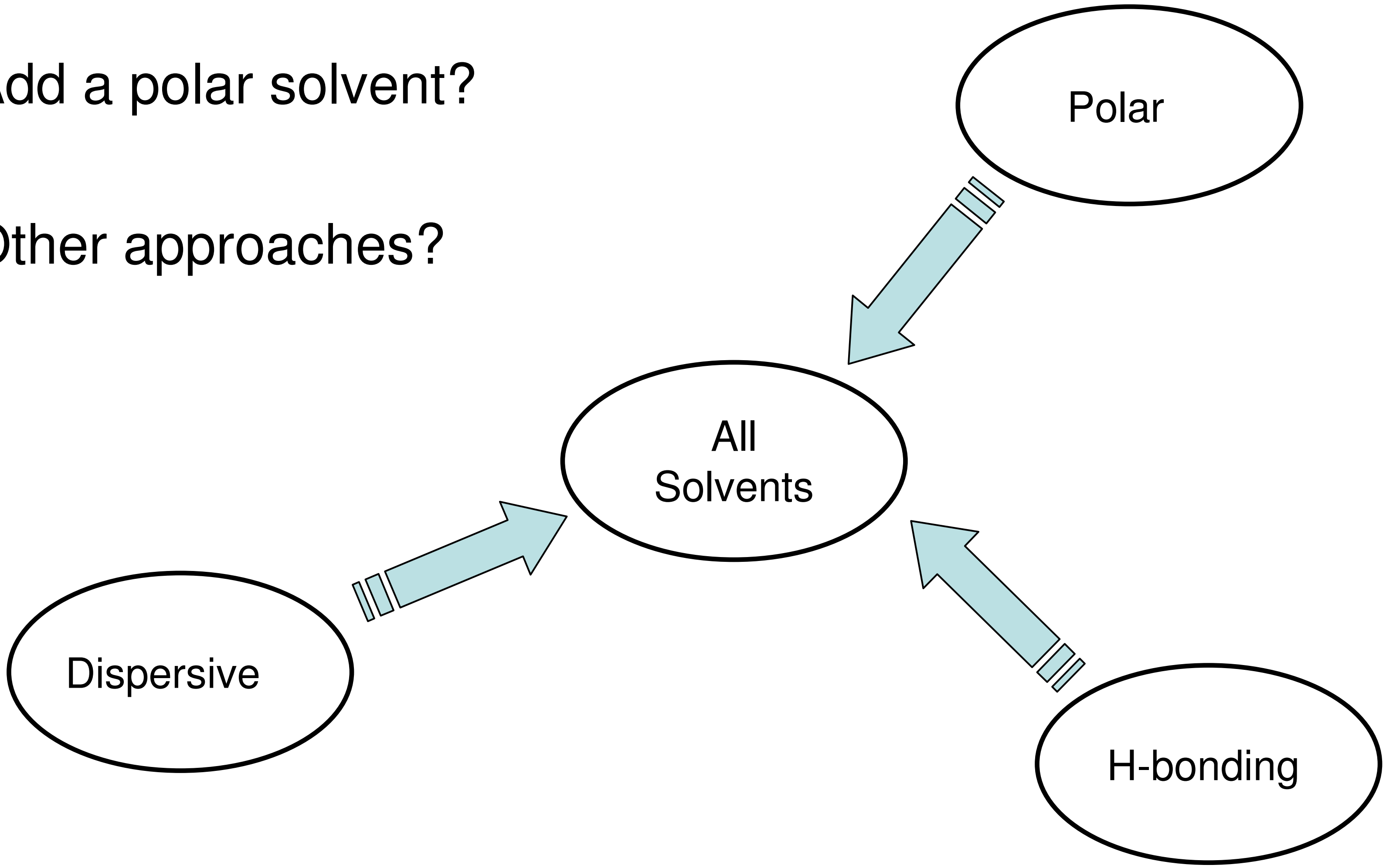
Solvent	a_{OH}	a_{CH3}	γ^∞ **exp.**	γ^∞ **pred.**
Water	1.7	0		13
Ethanol	0.296	0.704	16.53	13.1
Hexane	0	2.2		764

Extension to Other Solvents - Alcohols



Further Work

- Add a polar solvent?
- Other approaches?



Acknowledgements

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  - Prof. D. Ramjugernath
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  - DDBST GmbH

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