

EXTRAPOLATION OF INFINITE DILUTION ACTIVITY COEFFICIENT DATA FOR ALKANE SOLVENTS

Bruce Moller^a, Jürgen Rarey^{a,b,*}, Deresh Ramjugernath^a

^a Thermodynamics Research Unit, University of KwaZulu-Natal, Durban, 4041, South Africa; *Email: juergen@rarey.net

^b Industrial Chemistry, Carl von Ossietzky University Oldenburg, 26111 Oldenburg, FRG

Objective

- To increase the amount of data in the training set for the development of a new estimation method for γ_i^∞ in several simple solvents.
- Experimental data needed to be converted from several solvents in one family (alkanes, ketones & alcohols) to a single representative solvent (n-hexane, butanone & propanol)
- Abundance of γ_i^∞ data available in high molecular weight (low volatility) solvents from gas chromatography retention time measurements.
- Data for high boilers in low boiling solvents are scarce and difficult to measure but are often important in process design and simulation. They should be safely derived from data in high boiling solvents.

Test results for alkane solvents

- If one considers that, for alkane solvents at infinite dilution, the residual contributions to the activity coefficient are equivalent then the following expression holds:

$$\gamma_{i,sol1}^\infty = \gamma_{i,sol2}^\infty \frac{\gamma_{i,sol1}^{C,\infty}}{\gamma_{i,sol2}^{C,\infty}}$$

- Do the combinatorial expressions available in the literature correctly describe the dependence of γ_i^∞ of a specific solute on the size of the solvent molecule?

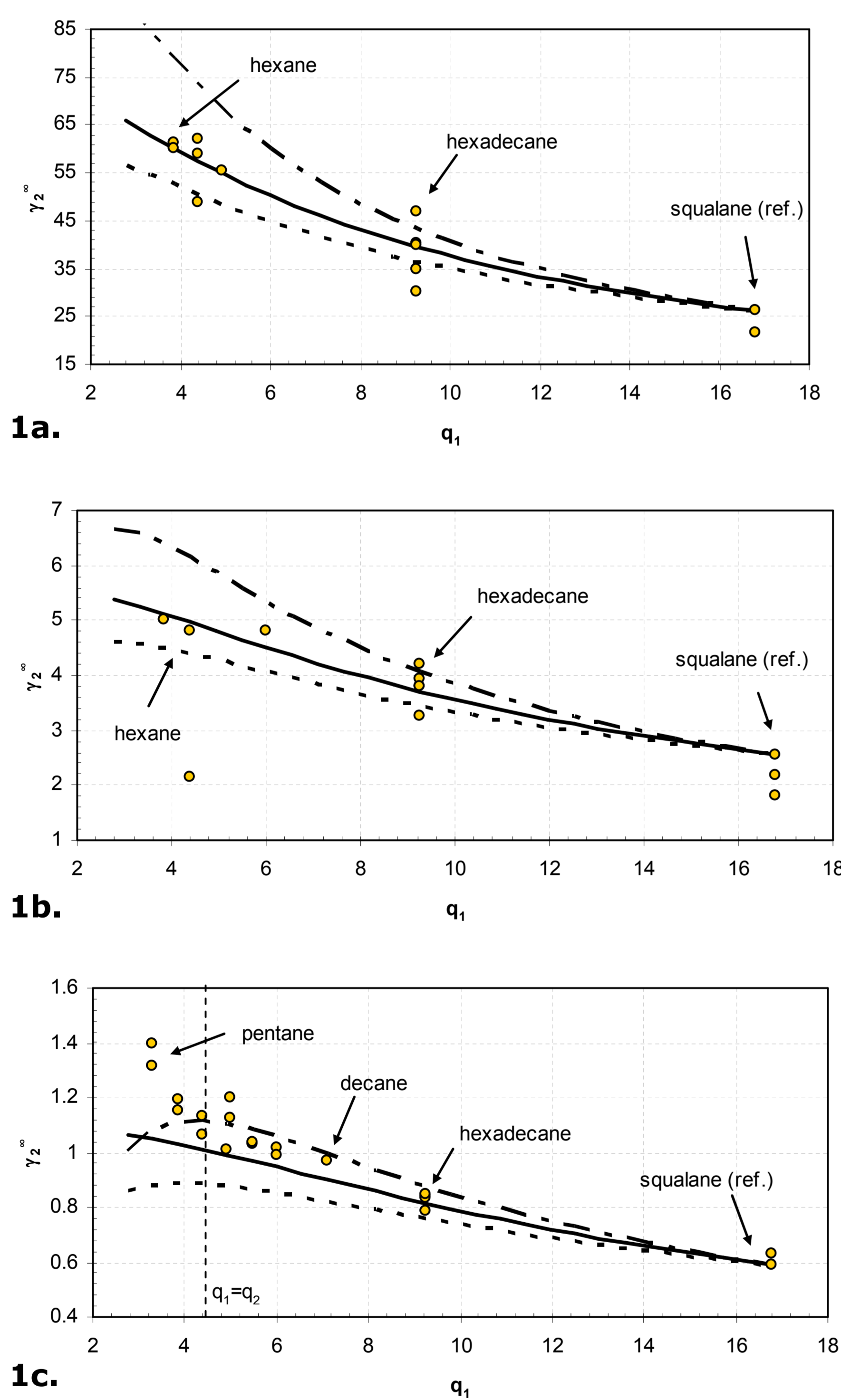


Figure 1. γ_2^∞ vs. q_1 for a. ethanone b. butanone and c. ethylcyclohexane (2) in alkane solvents(1) using squalane as the reference solvent at 298.15 K (• - data from the DDB [1], - - - SG combinatorial [2], ····· mod. UNIFAC combinatorial [3], — GK-FV combinatorial [4]).

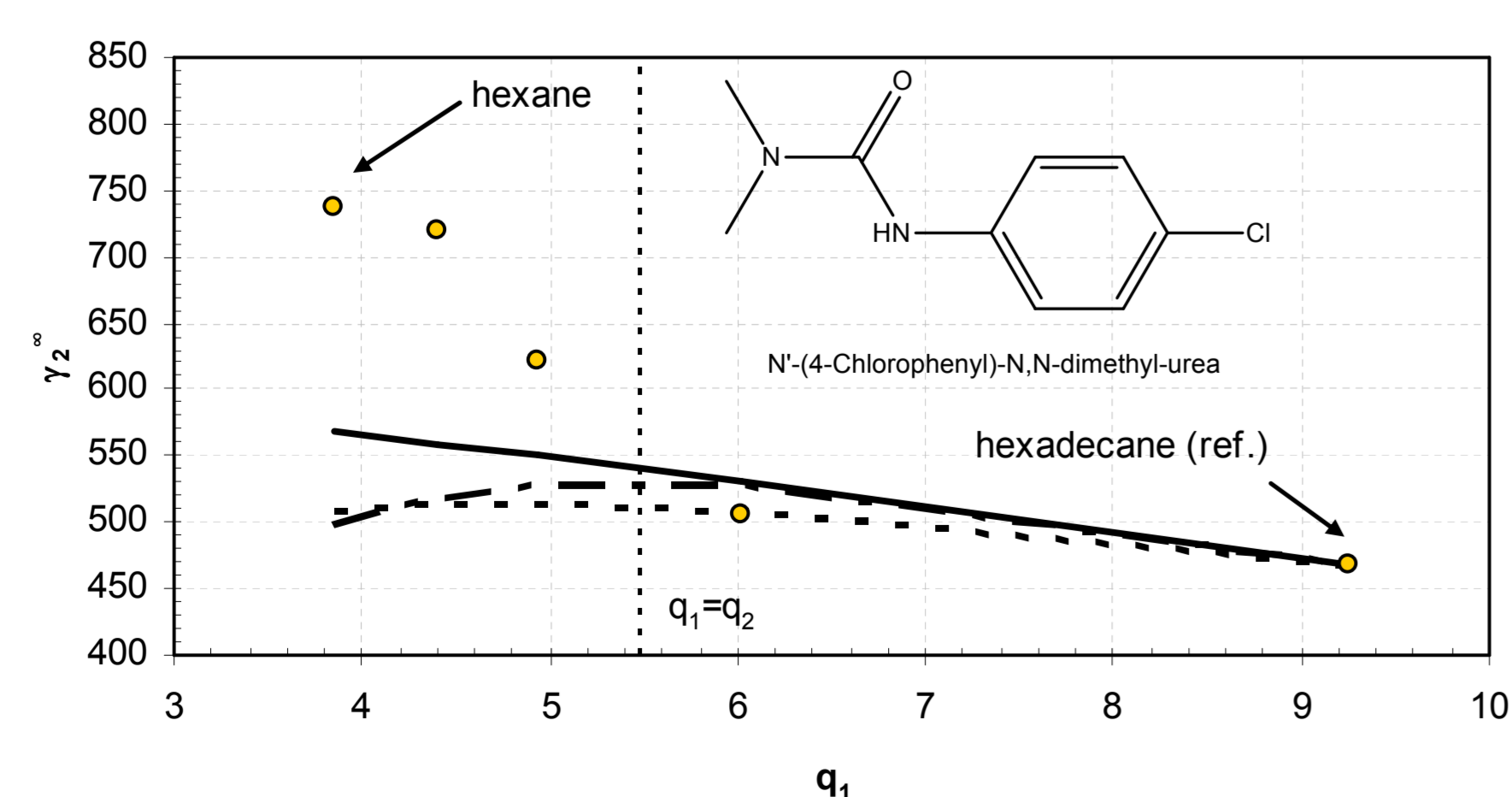


Figure 2. γ_2^∞ vs. q_1 for N-(4-chlorophenyl)-N,N-dimethyl-urea (2) in alkane solvents (1) using hexadecane as the reference solvent at 298.15 K (• - data calculated from solid-liquid equilibrium data from the DDB [1], - - - SG combinatorial [2], ····· mod. UNIFAC combinatorial [3], — GK-FV combinatorial [4]).

A new 'combinatorial' expression

- Tested combinatorial expressions deviate when the solute is larger than the solvent.
- This deviation is probably due to some cavitation contribution which is not captured by the combinatorial expression.
- This can be accounted for by adding an empirical term for the cavitation contribution:

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

$$\ln \gamma_2^{Cav,\infty} = \left(\frac{V_2^{FV}}{V_1^{FV}} - \frac{V_2^{IFV}}{V_1^{IFV}} \right)$$

$$V_i^{FV} = (V_i^L)^{2/3} - (V_i^G)^{2/3}$$

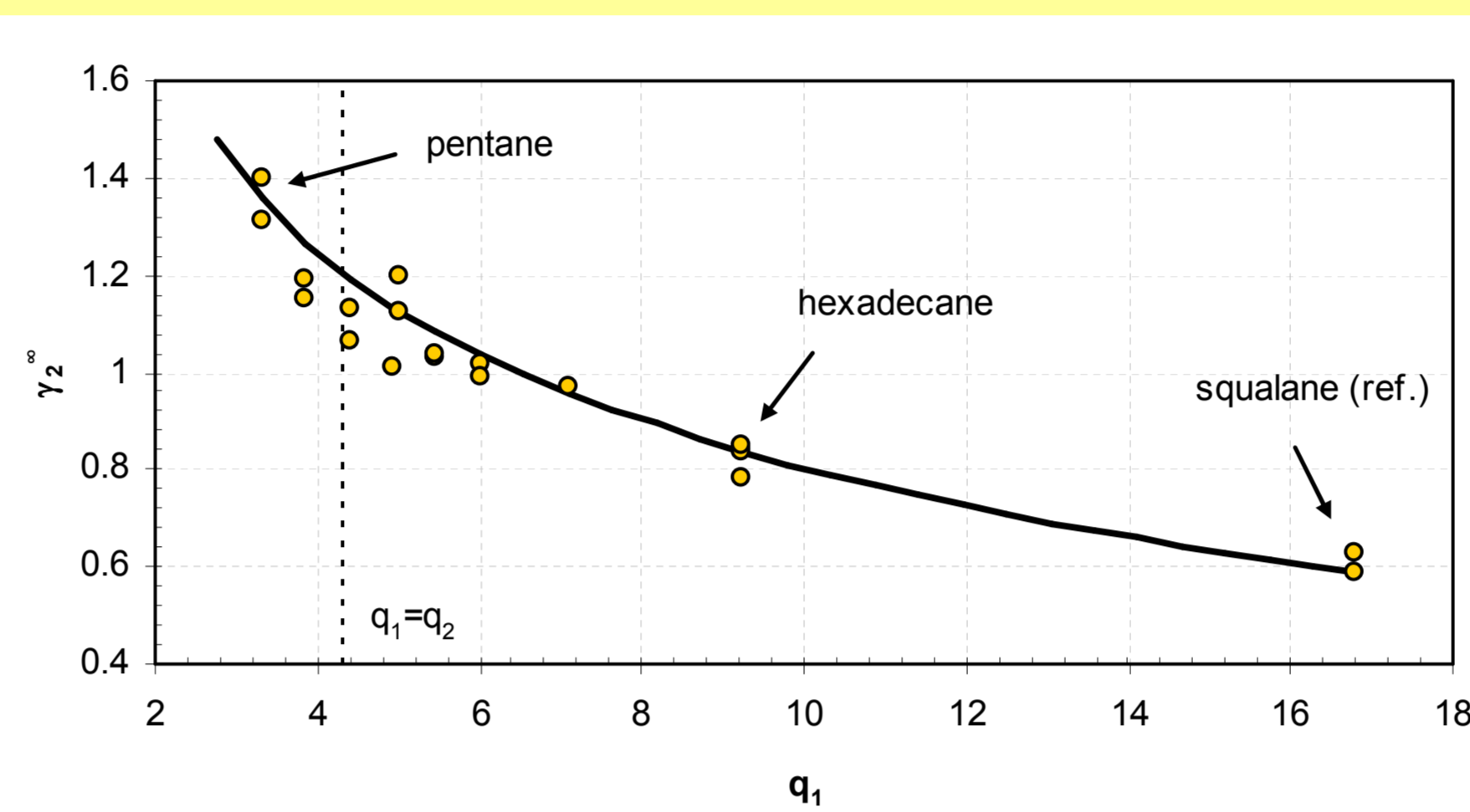


Figure 3. γ_2^∞ vs. q_1 for ethylcyclohexane (2) in alkane solvents(1) using squalane as the reference solvent at 298.15 K (• - data from the DDB [1], — new combinatorial expression).

- While this new expression improves the value of the combinatorial ratio the absolute value is incorrect, as illustrated in Figure 4.

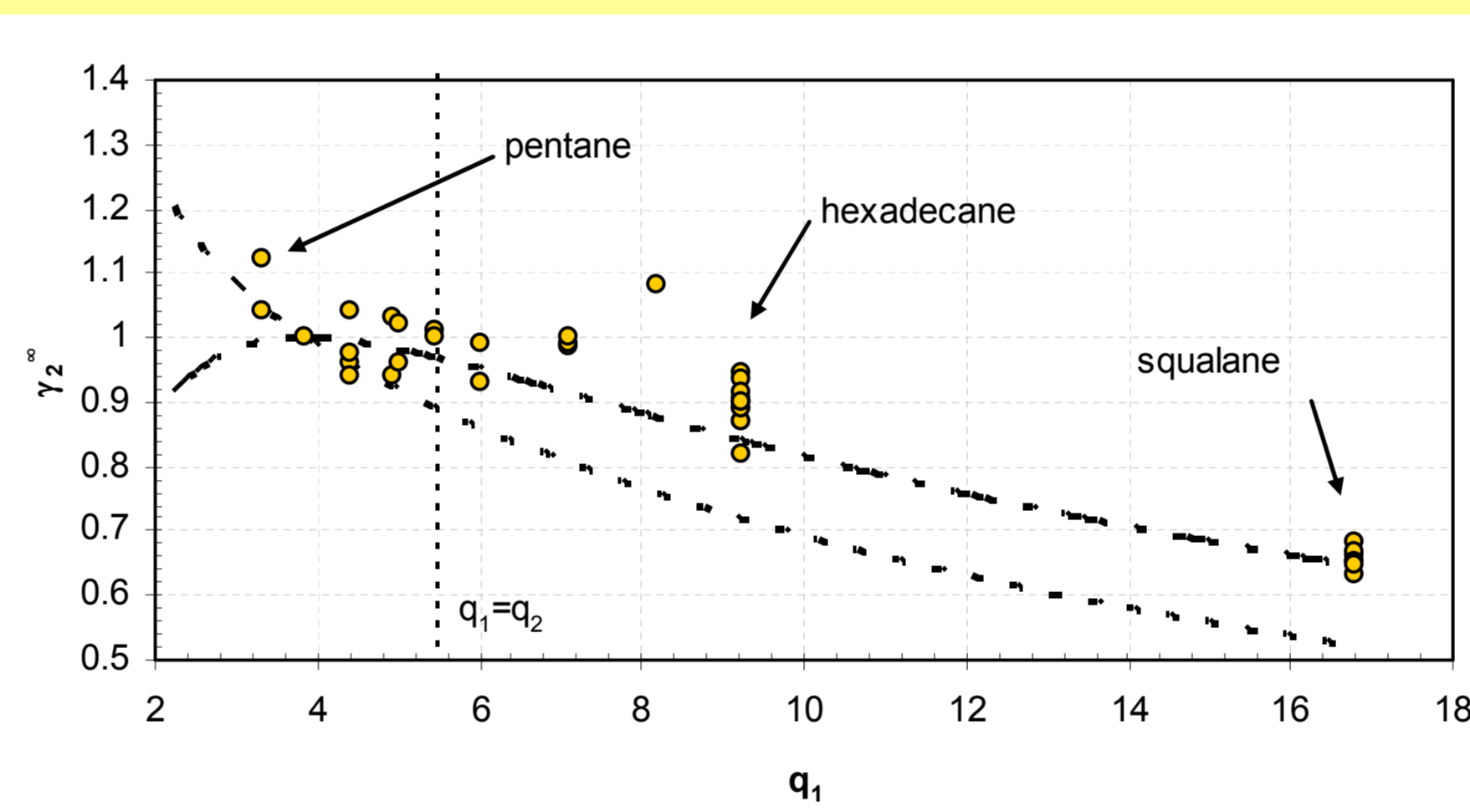


Figure 4. γ_2^∞ vs. q_1 for hexane (2) in alkane solvents(1) at 298.15 K (• - data from the DDB [1], - - - new uncorrected combinatorial, ····· mod. UNIFAC prediction).

- This deviation is due to the cavitation contribution and was empirically corrected by adding the following step function:

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

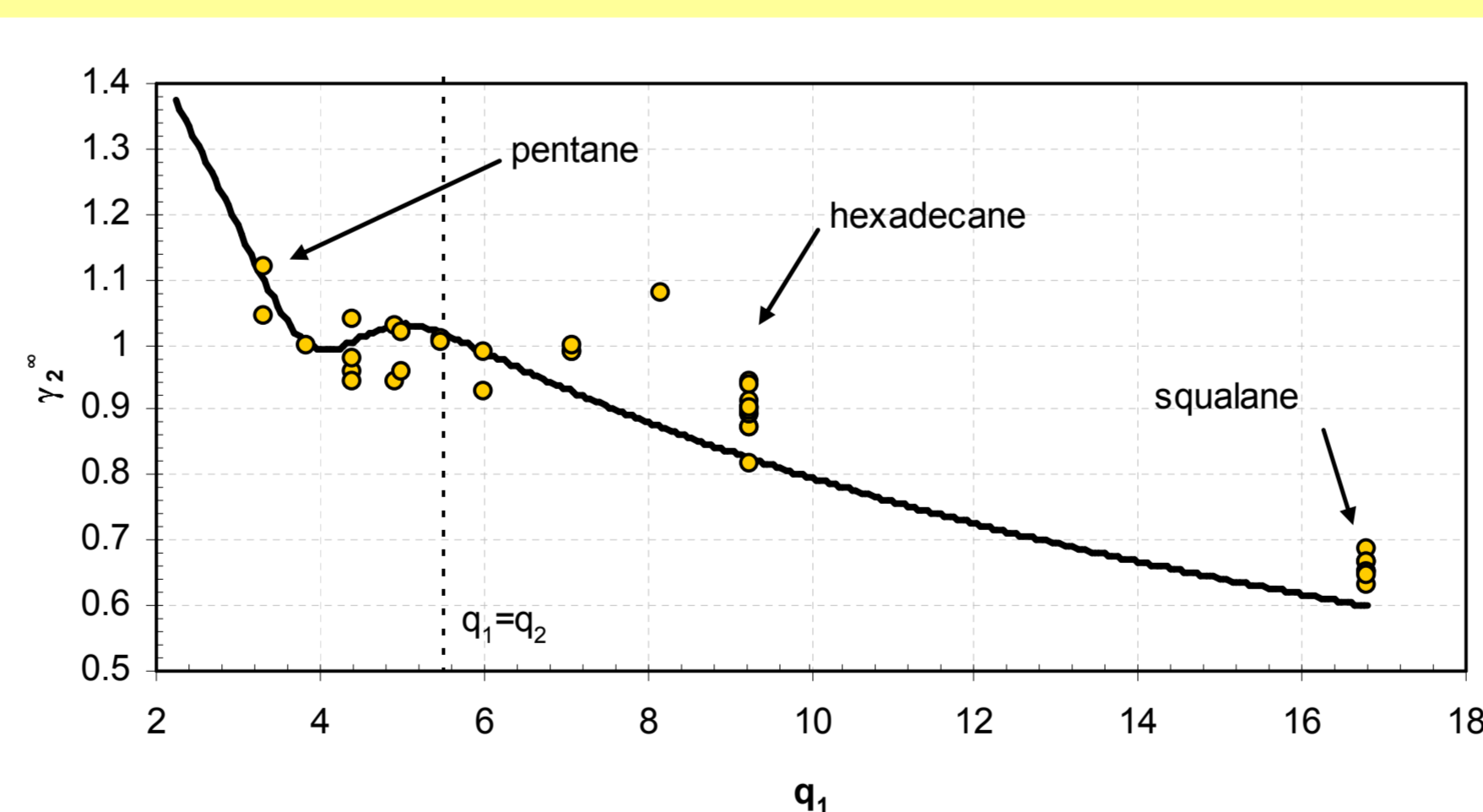


Figure 5. γ_2^∞ vs. q_1 for hexane (2) in alkane solvents(1) at 298.15 K (• - data from the DDB [1], — new corrected combinatorial).

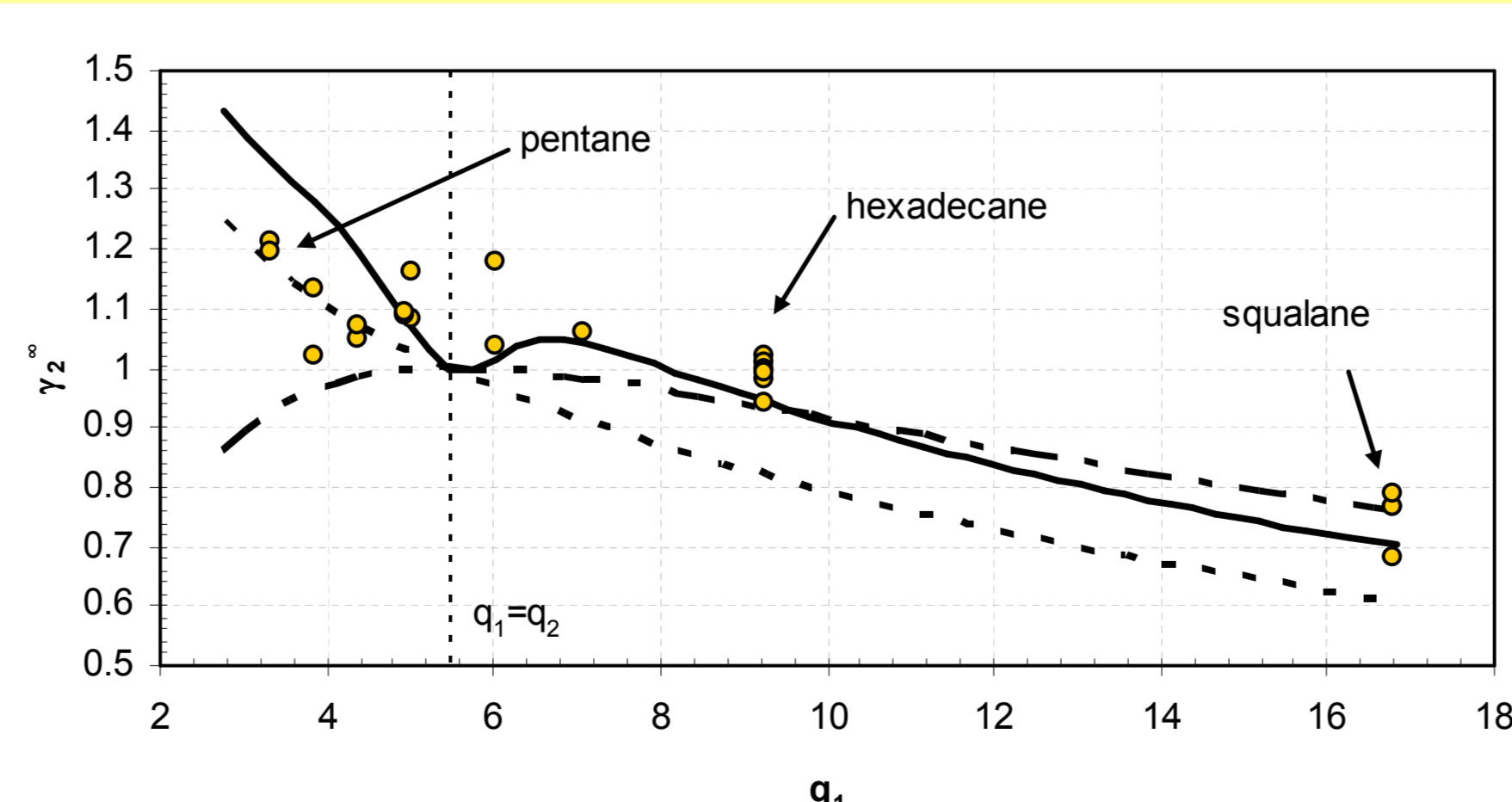


Figure 6. γ_2^∞ vs. q_1 for nonane (2) in alkane solvents(1) at 298.15 K (• - data from the DDB [1], — new corrected combinatorial, - - - new uncorrected combinatorial, ····· mod. UNIFAC prediction).

Results for alkane solvents

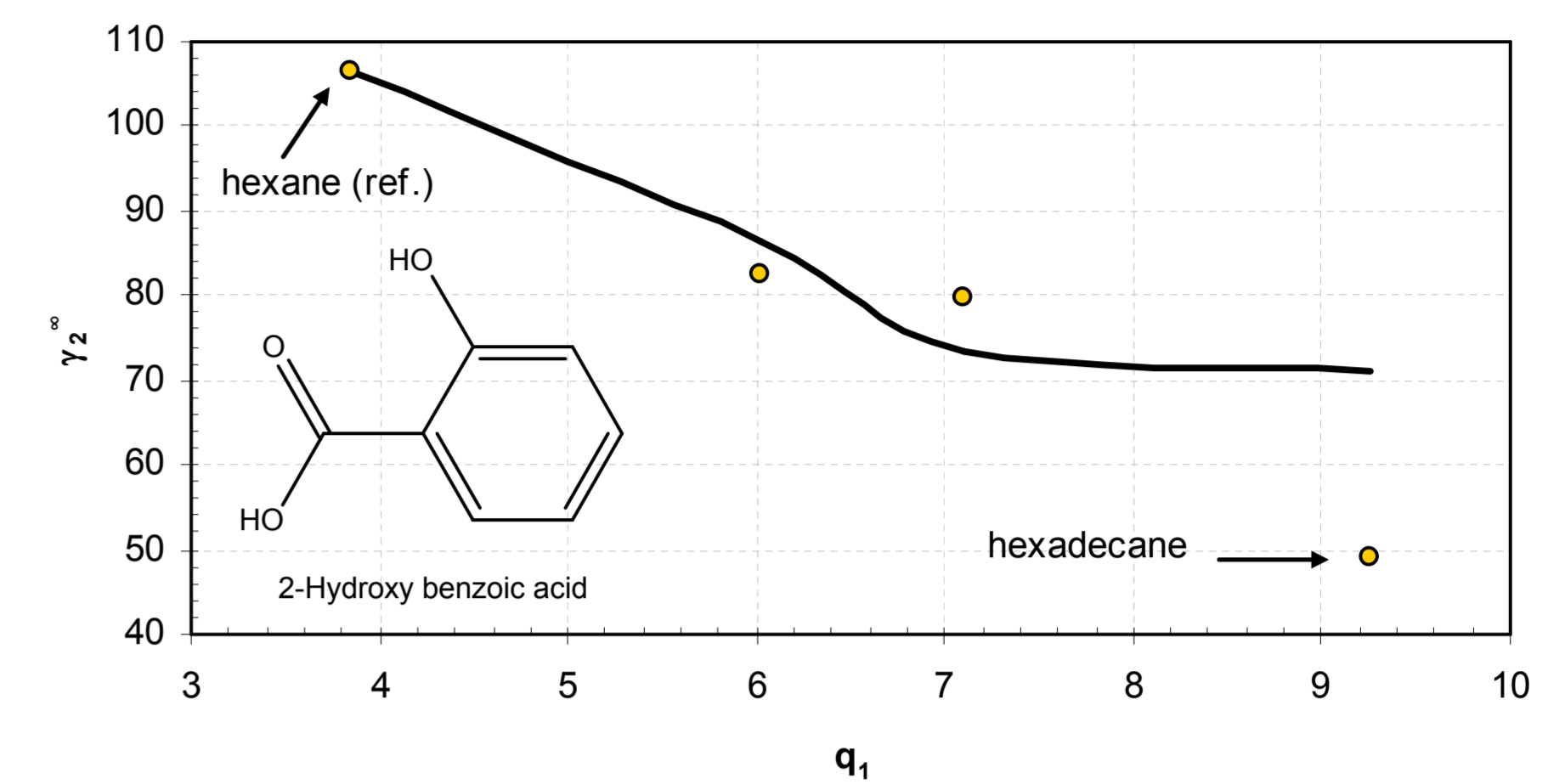


Figure 7. γ_2^∞ vs. q_1 for 2-hydroxy benzoic acid (2) in alkane solvents(1) using hexane as the reference solvent at 298.15 K (• - data calculated from solid-liquid equilibrium data from DDB [1], — new combinatorial expression).

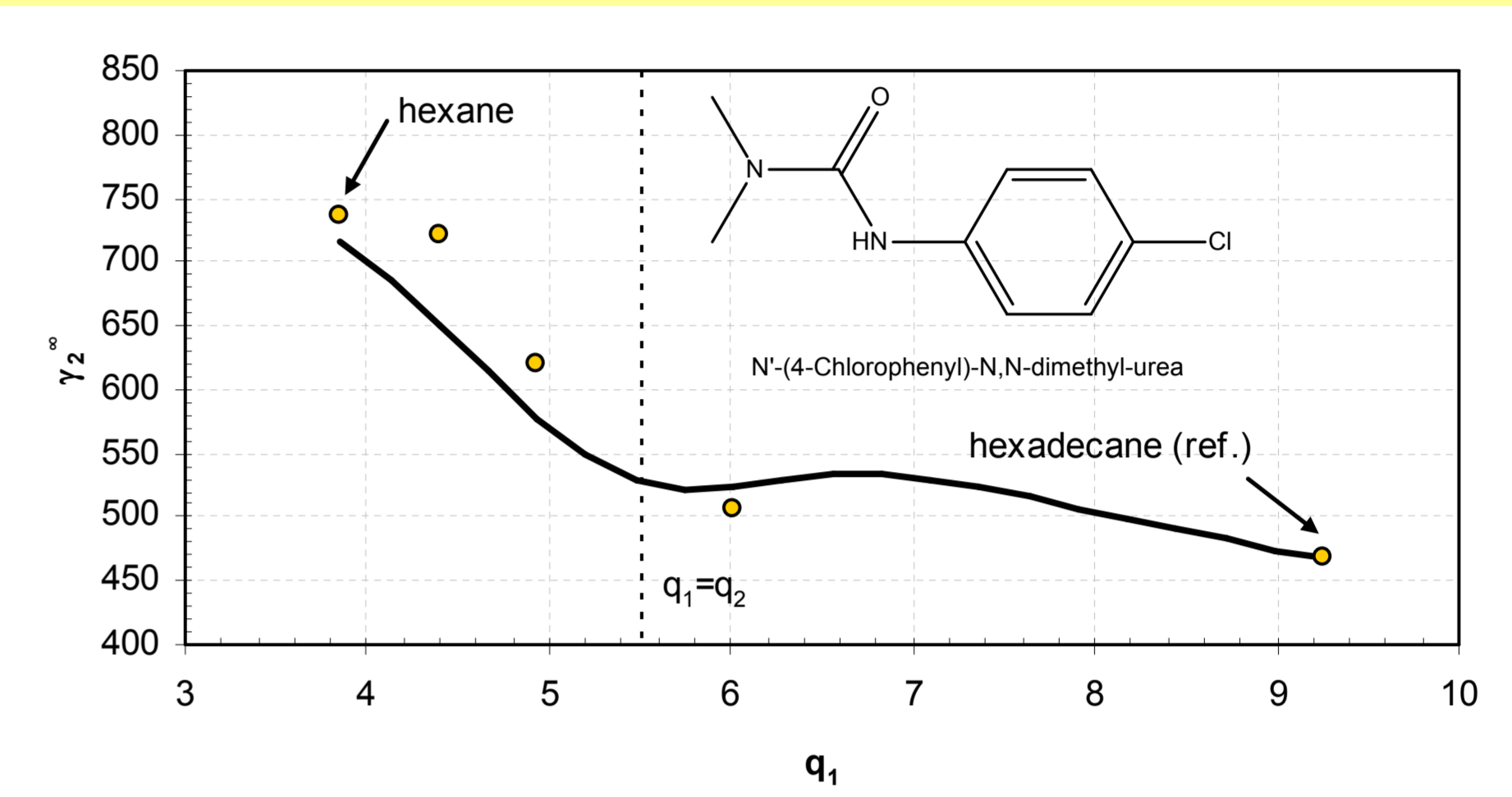


Figure 8. γ_2^∞ vs. q_1 for N-(4-chlorophenyl)-N,N-dimethyl-urea (2) in alkane solvents (1) using hexadecane as the reference solvent at 298.15 K (• - data calculated from solid-liquid equilibrium data from DDB [1], — new combinatorial expression).

Improvement of UNIFAC predictions

- Since the combinatorial expression proposed here improves the extrapolations in alkane solvents it was hoped that it could improve the predictions for UNIFAC for both alkane solvents and, more generally, for all solvents:

Table 1. Relative mean deviation (RMD) in $\ln \gamma$ when using the UNIFAC parameters with the original and the new combinatorial expression (comparisons made with data from the DDB [1], all data for water - i.e. water as a solute and solvent - were excluded and all data falling in the range $0.99 < \ln \gamma < 1.01$ were excluded as they greatly skew the percentage errors).

Combinatorial	RMD (%) in $\ln \gamma^\infty$	Number of data points
Original	101.2	29642
This work	82.3	29634

Conclusion and further research

- A method has been developed for the extrapolation of infinite dilution activity coefficient data from one alkane solvent to another.
- Estimation of γ_i^∞ data in some common solvents then interpolate/extrapolate to other less common solvents.

Acknowledgements

This work is based upon research supported by the South African Research Chairs Initiative of the Department of Science and Technology, NRF and BMBF (WTZ project). The authors would like to acknowledge DDBST GmbH for providing data and software support for this project. We especially thank Prof. J. Gmehling, the project leader of the WTZ-project.

References

- [1] Gmehling, J., Rarey, J., Menke, J., Dortmund Data Bank, Oldenburg (2008) <http://www.ddbst.com>
- [2] Guggenheim, E. A., Mixtures: The Theory of the Equilibrium Properties of Some Simple Classes of Mixtures, Solutions and Alloys. 1952, Oxford: Clarendon Press.
- [3] Weidlich, U., Gmehling, J., A Modified UNIFAC Model. 1. Prediction of VLE, h^E and γ^∞ . Ind. Eng. Chem. Res., 1987. **26**: p. 1372-1381.
- [4] Kontogeorgis, G. M., Fredenslund, A., Tassios, D. P., Simple Activity Coefficient Model for the Prediction of Solvent Activities in Polymer Solutions. Ind. Eng. Chem. Res., 1993. **32**: p. 362-372.