

# EXTRAPOLATION/INTERPOLATION OF INFINITE DILUTION ACTIVITY COEFFICIENT DATA BETWEEN SOLVENTS

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Whenever components are strongly diluted in a process stream or in a compartment in the environment, infinite dilution activity coefficient data play a vital role in modeling their phase equilibrium behavior. Although a large amount of these values is available in the open literature as well as from thermophysical data banks (such as the DDB), especially the behavior of high boiling solutes in low boiling solvents is often not known, partly due to difficulties in experimental determination.

To overcome this problem, work on a method for the extrapolation of infinite dilution activity coefficient data of a fixed solute in different solvents within one solvent family was started. This contribution will present results of a method applicable to any solute in a large variety of different saturated hydrocarbon compounds.

In group contribution  $g^E$  models such as UNIFAC and mod. UNIFAC the activity coefficient is calculated from:

- a combinatorial part (entropic contribution to  $g^E$  in the infinite temperature random mixture limit) and
- a residual part covering the enthalpic interactions between the structural groups

In case of alkane solvents, the residual term does not change when going from one solvent to another and therefore can be calculated from data for any (reference) solvent. Due to different size and shape of the alkanes, the combinatorial part will be different for each solvent. Several well known combinatorial expressions were evaluated and were found to produce poor extrapolations in many instances. Quite surprisingly, free-volume combinatorial expressions performed best even for the rather low molecular weight solvents used in this test. A new empirically modified free-volume expression is proposed which allows for accurate extrapolation. Empirical methods applicable to non-alkane solvents are also presented.

Keywords: Infinite dilution activity coefficients; prediction; combinatorial expression; alcohols; ketones; alkanes

## 1. RESULTS

### 1.1. Alkanes

The success of methods like UNIFAC has shown that the principle of solutions of groups does have practical application. It can therefore be assumed that a solute molecule at infinite dilution will only “see” the solvent groups around it. Since alkanes are all made up of  $sp^3$  carbons ( $CH_3$  UNIFAC group) it would make sense that the ratio of a solutes infinite dilution activity coefficient in two different alkane solvents should only in some way depend on the size and shape of the solvent molecules. (This reasoning applies to infinite dilution data since the solute molecule will only “see” solvent groups and not other solute groups). If it is assumed that the activity coefficient is only made

up a combinatorial (size/shape interactions) and a residual (energetic interactions) contribution then, since the residual contributions are equivalent, the following expression would result:

$$\frac{\gamma_{i,sol1}^{\infty}}{\gamma_{i,sol2}^{\infty}} = \frac{\gamma_{i,sol1}^{C,\infty}}{\gamma_{i,sol2}^{C,\infty}} \quad (1)$$

where the superscript *C* denotes the combinatorial expression and the subscripts *sol1* and *sol2* differentiate between any two alkane solvents. This expression can therefore be rearranged to give the infinite dilution activity coefficient in any alkane solvent relative to a known solvent:

$$\gamma_{i,sol1}^{\infty} = \gamma_{i,sol2}^{\infty} \frac{\gamma_{i,sol1}^{C,\infty}}{\gamma_{i,sol2}^{C,\infty}} \quad (2)$$

The Guggenheim-Staverman (SG) expression (Kikic et al. 1980; Lei et al. 2008) showed quite a large deviation when going from small to large solvents. The modified UNIFAC expression performed a bit better but tended to under-predict the activity coefficient when going from a large reference solvent to a small one (and *visa versa*). The free volume expression provides a very good prediction of the experimental data and can go from very big to very small solvents with a fair level of accuracy (usually within 10%). This success is somewhat surprising since free volume is almost never considered in non-polymer applications. The success of this term in this method could indicate that free volume does have an impact of the combinatorial contribution. An example of the usage of Eqn. (2) is shown in Fig. 1.

Initially when testing the method, quite accidentally, only solutes which were smaller than all of the solvents used were tested (this is due to the high availability of such data). However when the size of the solute became larger than the size of the solvent, the predictions started to show very large negative deviations. This is quite well illustrated in the example of ethylcyclohexane shown in Fig. 2. All three combinatorial expressions show much worse predictions as soon as the size of the solute ( $r_2$ ) becomes larger than the size of the solvent ( $r_1$ ). The larger the size of the solute the worse this error becomes.

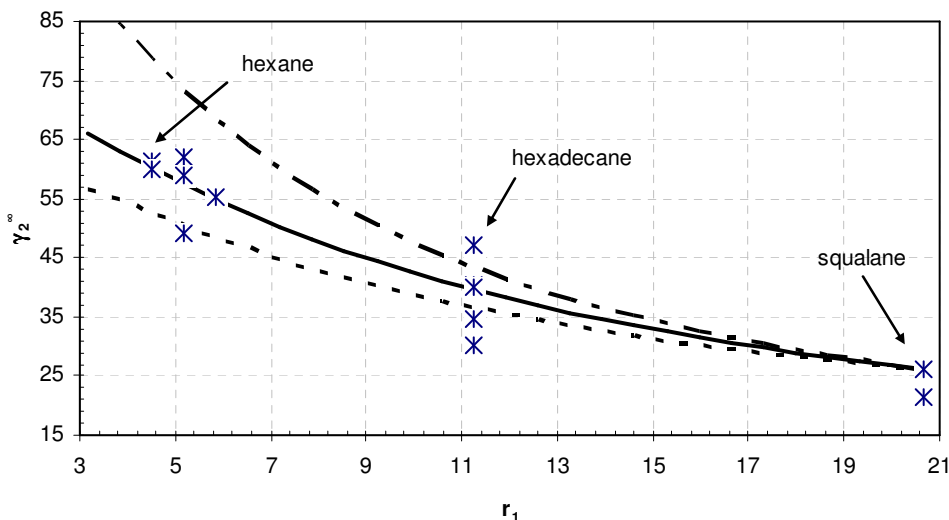


Fig. 1  $\gamma_2^{\infty}$  vs.  $r_1$  for ethanol(2) in alkane solvents(1) using squalane as the reference solvent at 298.15 K (x – data from the DDB (Gmehling et al. 2008), - - - SG combinatorial, ..... mod-UNIFAC combinatorial, — GK-FV combinatorial).

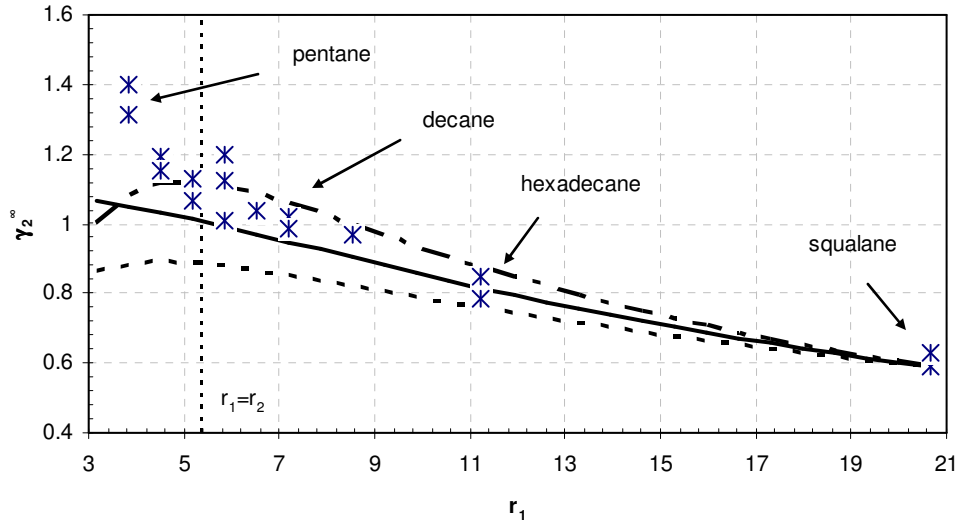


Fig. 2  $\gamma_2^\infty$  vs.  $r_1$  for ethylcyclohexane (2) in alkane solvents(1) using squalane as the reference solvent at 298.15 K (x – data from the DDB (Gmehling et al. 2008), - - - SG combinatorial, ..... mod-UNIFAC combinatorial, — GK-FV combinatorial).

This problem was solved by empirically modifying the GK-FV (Kontogeorgis et al. 1993) expression as follows:

$$\gamma_2^{C,\infty} = \exp \left( 1 - \frac{V_2^{iFV}}{V_1^{iFV}} + \ln \left( \frac{V_2^{iFV}}{V_1^{iFV}} \right) - 5q_2 \left( 1 - \frac{r_2/r_1}{q_2/q_1} + \ln \left( \frac{r_2/r_1}{q_2/q_1} \right) \right) \right) \quad (3)$$

$$V_i^{iFV} = (V_i)^{2/3} - (V_i^*)^{2/3} \quad (4)$$

This expression provides a much improved prediction for the large solutes in small solvents while still providing almost identical results for small solutes in larger solvents. The one problem with this empirical modification is that, while the ratio of the combinatorial expressions is correct, the absolute values change for the worse. This means that this combinatorial expression could not be used to accurately predict the activity coefficients of a mixture of alkanes. However if Eqn. (3) is multiplied by 1.2 the alkane solution predictions become much better and it in no way effect the extrapolations.

This method also provides a good method to test or develop combinatorial expressions. As mentioned above often combinatorial expressions are only developed by considering solutions of alkanes where the residual falls away. However if this approach is applied it provides a much broader scope and applicability while still remaining realistic.

### 1.2. Alcohols

Since the infinite dilution activity coefficient is by definition independent of concentration it can be assumed that it behaves like a pure component property. Therefore within the homologous series' it is assumed that the infinite dilution activity coefficient is made up of a hydrocarbon contribution and a functional group contribution (i.e. for the alcohols the contribution would be for the OH group):

$$\ln \gamma_{i,j}^\infty = a_{j,fun} \ln \gamma_{i,fun}^\infty + a_{j,CH_3} \ln \gamma_{i,CH_3}^\infty \quad (5)$$

where the subscript  $i$  refers to the solute,  $j$  refers to the solvent,  $fun$  refers to the function group and  $CH_3$  refers to the hydrocarbon contribution. The hypothetical infinite dilution activity coefficients in each contribution ( $\gamma_{i,fun}^\infty$  &  $\gamma_{i,CH_3}^\infty$ ) are the model parameters. For the alcohols, Eqn. (5) becomes:

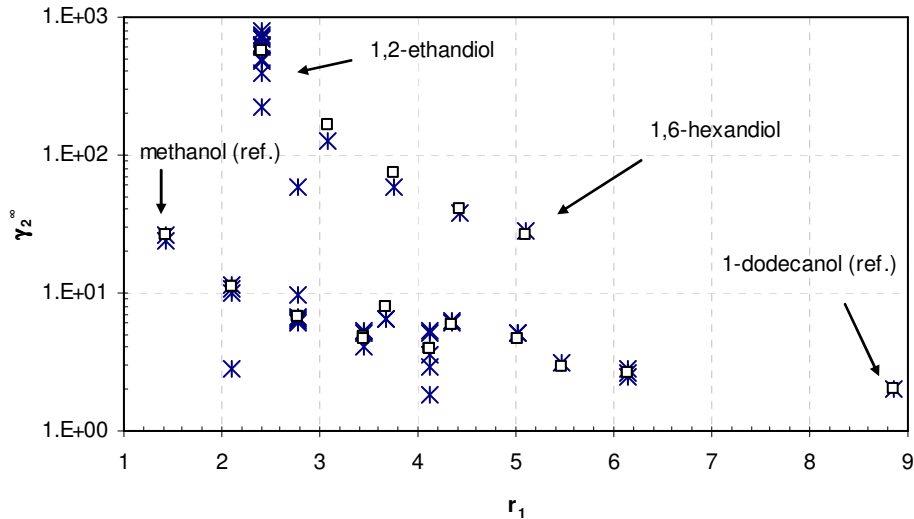
$$\gamma_{i,j}^\infty = (\gamma_{i,OH}^\infty)^{a_{j,OH}} (\gamma_{i,CH_3}^\infty)^{a_{j,CH_3}} \quad (6)$$

where the values for  $a_{j,OH}$  and  $a_{j,CH_3}$  are specified for each solvent as shown in Table 1.

**Table 1** The surface segments for the alcohol and ketone homologous series (all non-aromatic)  $q_{OH} = 0.584$  and  $q_{CO} = 0.64$ .

Solvent	$a_{j,fun}$	$a_{j,CH_2}$
<b>Alcohols</b>		
Water	1.8	0
Non-cyclic mono alcohols	$q_{OH} / q_j$	$1 - a_{j,fun}$
Non-cyclic diols	$3.1 \times q_{OH} / q_j$	$1 - a_{j,fun}$
Cyclic non-aromatic alcohols	$1.3 \times q_{OH} / q_j$	$1 - a_{j,fun}$
<b>Ketones</b>		
Non-aromatic ketone	$q_{CO} / q_j$	$1 - a_{j,fun}$

For the alcohols there is a large amount of infinite dilution data available which makes it convenient first-test for the method outlined above. Fig. 3 illustrates the general problem with infinite dilution data; there is a large scatter in the data with values sometimes ranging over one or two orders of magnitude. Therefore when data are reported in tables GLC data will be taken as superior or in the case of multiple GLC data the median will be reported. Generally the best results are obtained when there is a large alcohol (octanol, dodecanol etc.) and a small alcohol (water, methanol etc.) as a reference solvent.



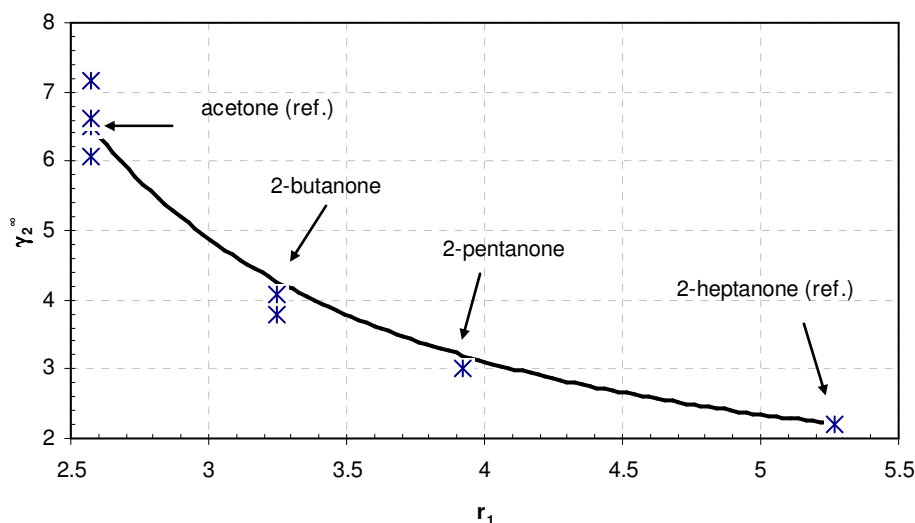
**Fig. 3**  $\gamma_2^\infty$  vs.  $r_1$  for hexane (2) in alcohol solvents(1) at 298.15 K with 1-dodecanol and methanol as the reference solvents (x – data from the DDB (Gmehling et al. 2008), □ – Eqn. (6)).

**Table 2** Predicted and experimental data for various solutes (2) in non-aromatic alcohol solvents (1) (predictions carried out using Eqn. (6) with two reference solvents denoted by \*, data from the DDB (Gmehling et al. 2008), TMS = tetramethylstannane)

Solute (2) Temperature	TMS 298.15 K		Ethyl iodide 298.15 K		2-Butanone 298.15 K		1,4-Dioxane 298.15 K		Propylene 290 K	
	$\gamma_2^{\text{exp}}$	$\gamma_2^{\text{pred}}$	$\gamma_2^{\text{exp}}$	$\gamma_2^{\text{pred}}$	$\gamma_2^{\text{exp}}$	$\gamma_2^{\text{pred}}$	$\gamma_2^{\text{exp}}$	$\gamma_2^{\text{pred}}$	$\gamma_2^{\text{exp}}$	$\gamma_2^{\text{pred}}$
1,2-Ethanediol	-	-	-	-	8.4	4.8	4.8	2.4	-	-
1-Butanol	10.7	10.7*	3.2	3.2*	2.1	2.3	2.4	2.1	3.0	2.9
1-Dodecanol	-	-	-	-	-	-	-	-	-	-
1-Octanol	-	-	-	-	2.1	2.1*	2.1	2.1*	-	-
1-Pentanol	-	-	-	-	111.2	2.2	-	-	2.6	2.6*
1-Propanol	15.0	15.8	3.9	3.7	2.3	2.4	-	-	-	-
2-Propanol	12.7	15.9	3.8	3.7	-	-	-	-	3.7	3.5
2-Propen-1-ol	-	-	-	-	-	-	-	-	4.7	3.8
3-Methyl-1-butanol	-	-	2.3	2.8	1.8	2.2	2.1	2.1	-	-
3-Methyl-3-buten-1-ol	-	-	-	-	-	-	-	-	3.0	2.6
Ethanol	26.6	29.1	5.0	4.7	2.6	2.6	-	-	-	-
Methanol	65.0	84.3	8.0	7.3	2.4	3.0	-	-	7.3	7.3*
tert-Butanol	4.7	10.2	4.0	3.1	1.7	2.3	1.6	2.1	-	-
tert-Pentanol	-	-	-	-	-	-	-	-	2.3	2.6
Water	7.6E+07	7.6E+07*	2192.0	2192.0*	27.8	27.8*	5.4	5.4*	-	-

### 1.3. Ketones

As with the alcohols two reference solvents are required for the ketones since there are two different contributions. Unfortunately, unlike with the alcohols, there are not a many data available with which to make model tests, Fig. 4 shows the example of hexane for which there was a fair amount of data available. As with the alcohols the interpolation is fairly good.



**Fig. 4**  $\gamma_2^{\infty}$  vs.  $r_1$  for hexane (2) in ketone solvents(1) at 298.15 K ( x – data from the DDB (Gmehling et al. 2008), — Eqn. (5)).

In all the examples that have been show so far the infinite dilution activity coefficient decreases with the increasing size of the solute. This is, however, not necessarily the case. Fig. 5 shows the data for water in ketone solvents; in this example the size of the infinite dilution activity coefficient increases with increasing solvent size. The reason for this is that as the hydrophobic chain of the solvent increases the solvent becomes more hydrophobic and therefore one would expect the infinite dilution activity of hydrophilic solutes in the mixture to increase. This effect is

accounted for in the model by making the hydrophobic contribution to  $\gamma_i^\infty$  larger (i.e. the regressed value of  $\gamma_{i,CH_3}^\infty$  will be larger than the value of  $\gamma_{i,CO}^\infty$ ).

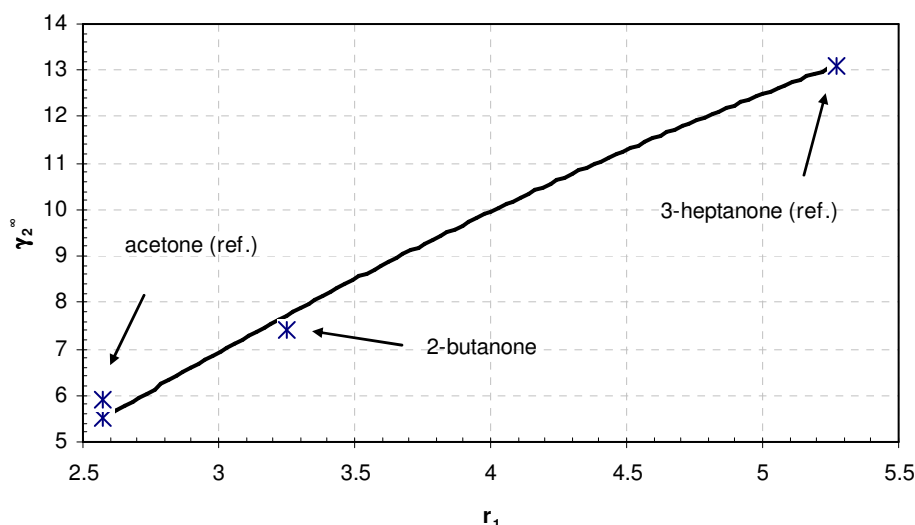


Fig. 5  $\gamma_2^\infty$  vs.  $r_1$  for water (2) in ketone solvents(1) at 333.15 K (x – data from the DDB (Gmehling et al. 2008), — Eqn. (5)).

## 2. CONCLUSION

Methods have been developed which allow the transformation of infinite dilution activity coefficient data for a single solute from one solvent to another. For alkane solvents a new method for testing combinatorial expressions has been developed, as well as a new combinatorial expression. When dealing with homologous series' a new method has been developed which allows for the interpolation of infinite dilution data based on two reference solvents.

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