

Extrapolation/Interpolation of Infinite Dilution Activity Coefficient Data between Solvents

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Abstract

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 (Sandler 1996). Although a large amount of these values are available in the open literature, as well as from thermophysical property data banks such as the DDB (Gmehling et al. 2008), typically 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.

For group contribution g^E models such as UNIFAC and mod. UNIFAC (Kikic et al. 1980; Lei et al. 2008) 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 the 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

Introduction

Activity coefficient data is necessary for the understanding and design of many unit operations in chemical engineering (crystallization, distillation, liquid-liquid extraction etc.). Very often (but not always) the maximum value of the activity coefficient occurs at the infinite dilution value, which is the limit of the activity coefficient as the concentration of the solute tends towards zero. The infinite dilution activity coefficient is therefore a convenient way to gauge the suitability of a solvent for, as an example, liquid-liquid extraction. The main methods for measuring infinite dilution activity coefficient data are Gas-Liquid Chromatography (GLC), static methods, ebulliometric and dilutor techniques (Eckert et al. 1981; Sandler 1996; Krummen et al. 2000). The disadvantages with performing experimental measurements are that the components need to be synthesized and for some systems which large (typically low volatility) solutes and small (typically volatile) solvents the measurements

can become very difficult. In this paper a method is proposed for the extrapolation of infinite dilution activity data within a homologous series from one solvent to another solvent, and extrapolation between homologous series’.

Results

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 solute’s 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 then be re-arranged to give the infinite dilution activity coefficient in any alkane solvent relative to a known solvent:

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

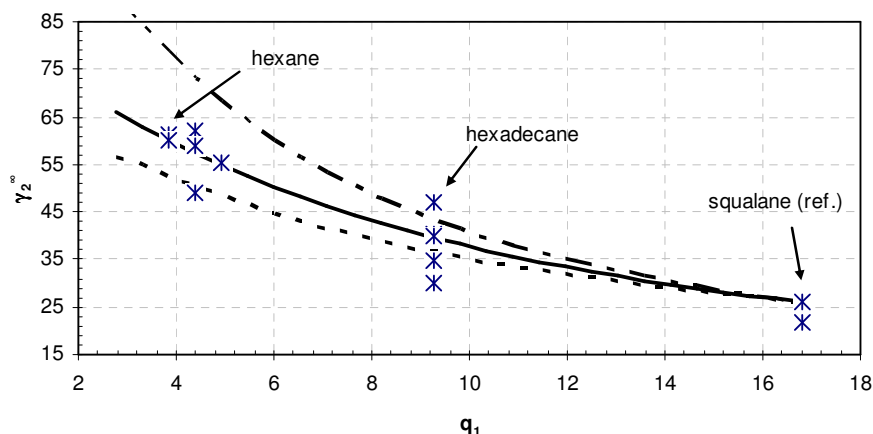


Figure 1: γ_2^{∞} vs. q_1 for ethanol(2) in alkane solvents(1) using squalane as the reference solvent at 298.15 K (x – data from the DDB (Gmehling et al. 2008), - - - SG combinatorial, mod-UNIFAC combinatorial, — GK-FV combinatorial).

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 on the combinatorial contribution. An example of the usage of Eqn. (2) is shown in Figure 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 well illustrated in the example of ethylcyclohexane shown in Figure 2. All three combinatorial expressions show much worse predictions as soon as the size of the solute (q_2) becomes larger than the size of the solvent (q_1). The larger the size of the solute the worse this error becomes.

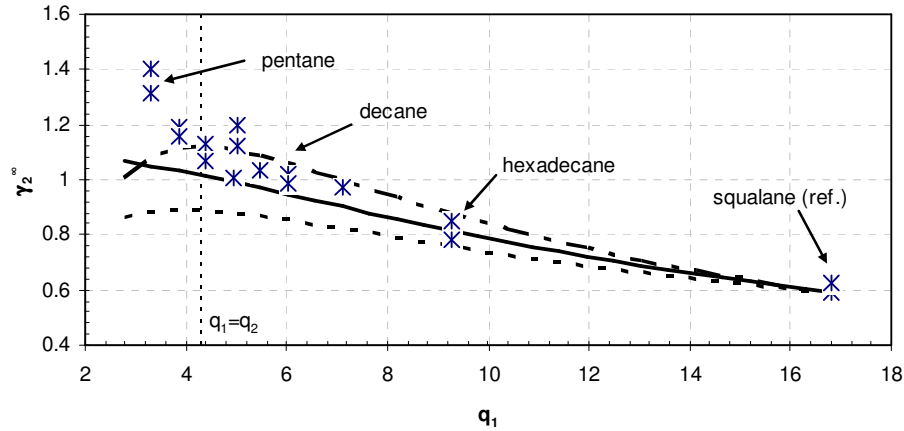


Figure 2: γ_2^∞ vs. q_1 for ethylcyclohexane (2) in alkane solvents(1) using squalane as the reference solvent at 298.15 K (x – data from the DDB (Gmehling et al. 2008), - · - · - SG combinatorial, ····· mod-UNIFAC combinatorial, — GK-FV combinatorial).

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

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

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

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 affects 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.

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 ($\gamma_{i,fun}^{\infty}$ & γ_{i,CH_3}^{∞}) are the model parameters. For the alcohols, Eqn. (5) becomes:

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

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

Table 1: 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}
Alcohols		
Water	1.8	0
Non-cyclic mono alcohols	q_{OH} / q_j	$1 - a_{j,fun}$
Non-cyclic diols	$3 \times q_{OH} / q_j$	$1 - a_{j,fun}$
Cyclic non-aromatic alcohols	$1.3 \times q_{OH} / q_j$	$1 - a_{j,fun}$
Hexane	0	2
Ketones		
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 a convenient first-test for the method outlined above. Figure 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.

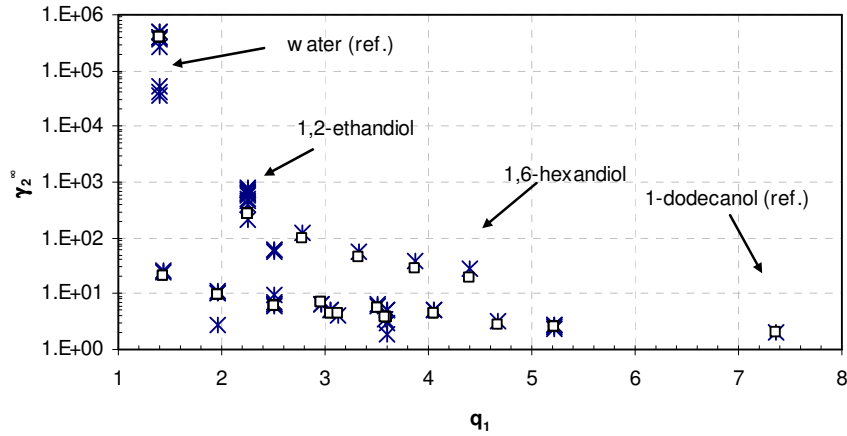


Figure 3: γ_2^∞ vs. q_1 for hexane (2) in alcohol solvents(1) at 298.15 K with 1-dodecanol and water as the reference solvents (x – data from the DDB (Gmehling et al. 2008), \square – Eqn. (6)).

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))

Solute(2)	Ethyl iodide		2-Butanone		1,4-Dioxane		Toluene	
	298.15 K		298.15 K		298.15 K		333.15 K	
Solvent(1)	γ_2^{exp}	γ_2^{pred}	γ_2^{exp}	γ_2^{pred}	γ_2^{exp}	γ_2^{pred}	γ_2^{exp}	γ_2^{pred}
Water	2192.0	2192.0*	27.8	26.2*	5.4	5.4*	6944.4	6944.4*
1,2-Ethandiol	-	-	8.4	4.9	4.8	5.9	50.4	48.3
Methanol	8.0	6.9	2.4	3.3	-	-	8.8	8.4
Ethanol	5.0	4.4	2.6	3.0	-	-	5.6	5.0
1-Propanol	3.9	3.4	2.3	2.8	-	-	-	-
2-Propanol	3.8	3.4	-	-	-	-	-	-
1-Butanol	3.2	2.9	2.1	2.7	2.4	2.1	5.1	3.1
tert-Butanol	4.0	2.9	1.7	2.7	1.6	2.1	-	-
1-Pentanol	-	-	111.2	2.6	-	-	-	-
3-Methyl-1-butanol	2.3	2.6	1.8	2.6	2.1	2.0	-	-
1-Octanol	-	-	2.3	2.5	2.1	2.0	-	-
1-Dodecanol	-	-	-	-	-	-	1.5	1.8
Hexane	1.9	1.9*	5.0	5.0*	3.95	3.95*	1.56	1.56*

Ketones

As with the alcohol interpolation, two reference solvents are required for the ketone interpolation since there are two different contributions. Unfortunately, unlike with the alcohols, there are relatively small amounts of data available with which to make model tests. Figure 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.

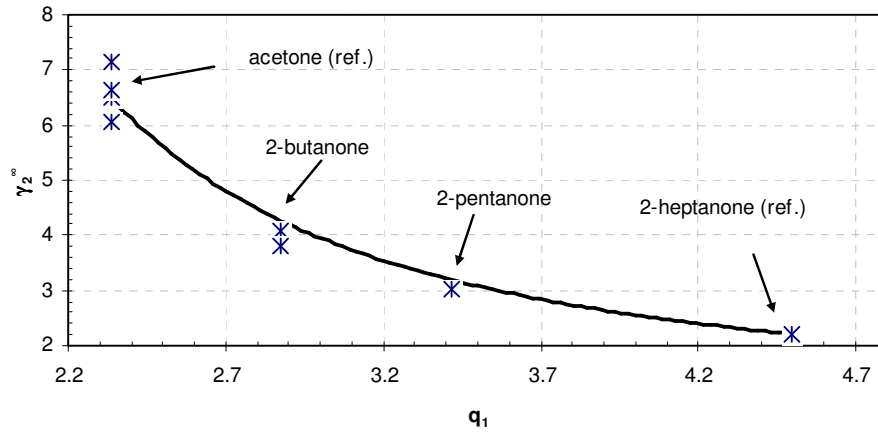


Figure 4: γ_2^∞ vs. q_1 for hexane (2) in ketone solvents(1) at 298.15 K (x – data from the DDB (Gmehling et al. 2008), — Eqn. (5)).

In all the examples that have been shown so far, the infinite dilution activity coefficient decreases with the increasing size of the solute. This is, however, not necessarily the case. Figure 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 γ_i^∞ larger (i.e. the regressed value of γ_{i,CH_3}^∞ will be larger than the value of $\gamma_{i,CO}^\infty$).

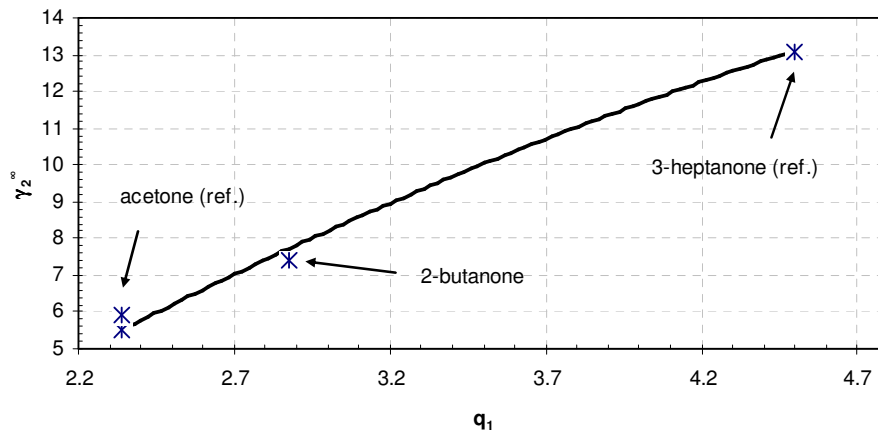


Figure 5: γ_2^∞ vs. q_1 for water (2) in ketone solvents(1) at 333.15 K (x – data from the DDB (Gmehling et al. 2008), — Eqn. (5)).

Conclusion

A method has been developed for interpolating the infinite dilution activity coefficient based on two reference solvents within a homologous series or four reference solvents if the general approach is applied. This method is not only useful for obtaining estimates but could also be used to check experimental data for the correct trends.

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