

Extrapolation of Infinite Dilution Activity Coefficient Data for Alkane Solvents

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Abstract

The determination of the infinite dilution activity coefficient can be carried out in a variety of ways. The disadvantages, however, with performing experimental measurements are that the components need to be synthesized and for some systems with large (high boiling) solutes and small (low boiling) solvents the measurements can become very difficult.

To overcome this problem, work on a method for the extrapolation of infinite dilution activity coefficient data of a fixed solute in different alkane solvents was started. In group contribution g^E models such as UNIFAC and modified UNIFAC (Kikic et al. 1980; Lei et al. 2008), the activity coefficient is calculated from:

- a combinatorial part (size/shape interactions) and
- a residual part covering the enthalpic interactions between the structural groups

In the case of solutes at infinite dilution in 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. However, due to differences in the size and shape the combinatorial part will be different for each alkane 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 solutes used in this test.

A new empirically modified free-volume expression is proposed which allows for accurate extrapolation. Tests were carried on some systems which contain large molecules (activity coefficient data extracted from solid-liquid equilibrium data). In most cases extrapolations were within 10% of the experimental findings and safely within or close to the scatter of literature.

Keywords: Infinite dilution activity coefficients; prediction; alkanes

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 solutes and small solvents the measurements can become very difficult. In this paper a

method is proposed for the extrapolation of infinite dilution activity data from one alkane solvent to another solvent.

Results

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 in some way only 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 of 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 re-arranged to give the infinite dilution activity coefficient in any alkane solvent relative to a known solvent:

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

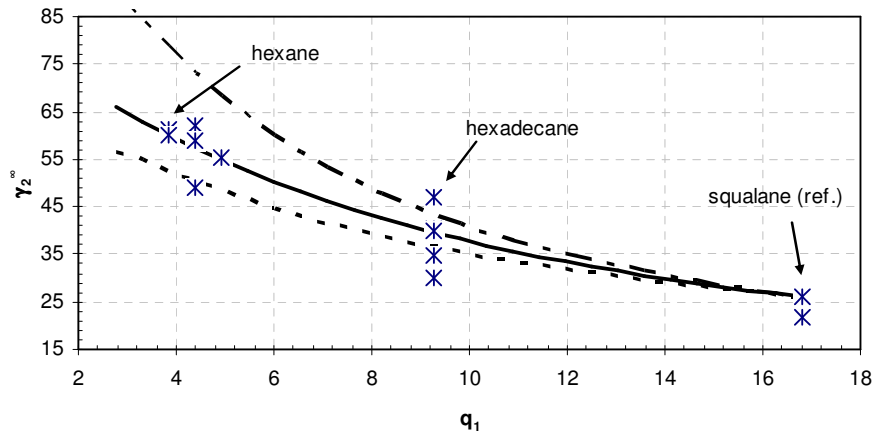


Figure 1: γ_2^{∞} vs. q_1 for ethanol(2) in alkane solvents(1) using squalane as the reference solvent at 298.15 K (x – data from the DDB (Gmehling et al. 2008), $- - -$ SG combinatorial, \cdots mod-UNIFAC combinatorial, $—$ GK-FV combinatorial).

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 *vice 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 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 quite 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.

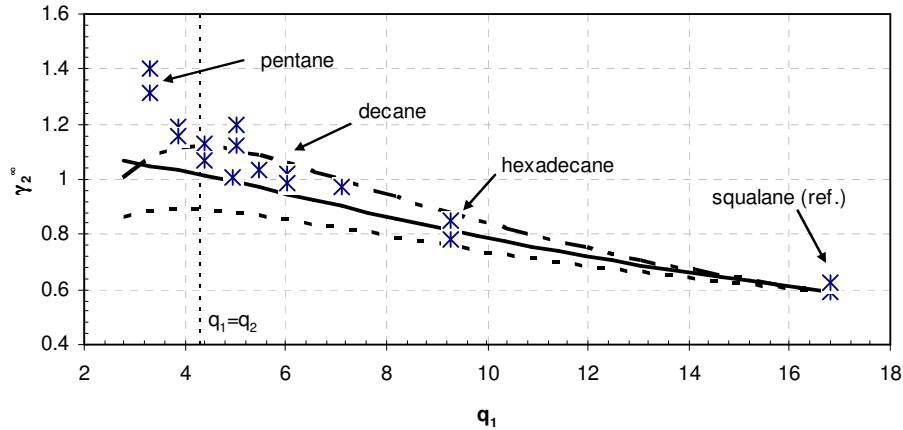


Figure 2: γ_2^∞ vs. q_1 for ethylcyclohexane (2) in alkane solvents (1) using squalane as the reference solvent at 298.15 K (x – data from the DDB (Gmehling et al. 2008), --- SG combinatorial, mod-UNIFAC combinatorial, — GK-FV combinatorial).

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. During the testing of the combinatorial expressions it was noted that the combinatorial ratio could be represented by the following simplified expression:

$$\frac{\gamma_{i,sol1}^{C,\infty}}{\gamma_{i,sol2}^{C,\infty}} = \left(\frac{r_{sol2}}{r_{sol1}} \right)^{0.6} \quad (5)$$

The huge advantage of this expression is that when combined with Eqn. (2), extrapolations can be made for any solute with no volume data needed for the solute. In order to test the general applicability of the method to systems with large solutes and smaller solvents some extrapolations were done on infinite dilution activity data extracted from solid-liquid equilibrium data. These plots are shown in Figure 3 and Figure 4; hexane is used as a reference solvent in both cases since this is the data which is more readily available in literature.

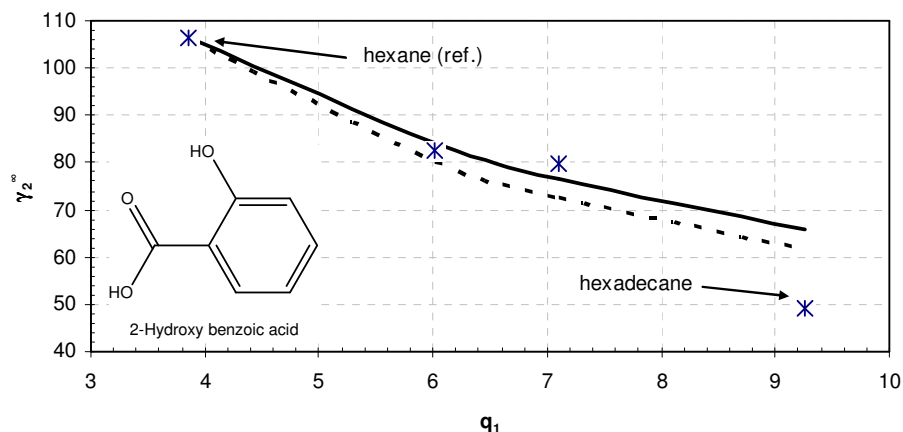


Figure 3: γ_2^∞ vs. q_1 for 2-hydroxy benzoic acid (2) in alkane solvents(1) using hexane as the reference solvent at 298.15 K (x – data from the DDB (Gmehling et al. 2008), — Eqn.(3), --- Eqn.(5)).

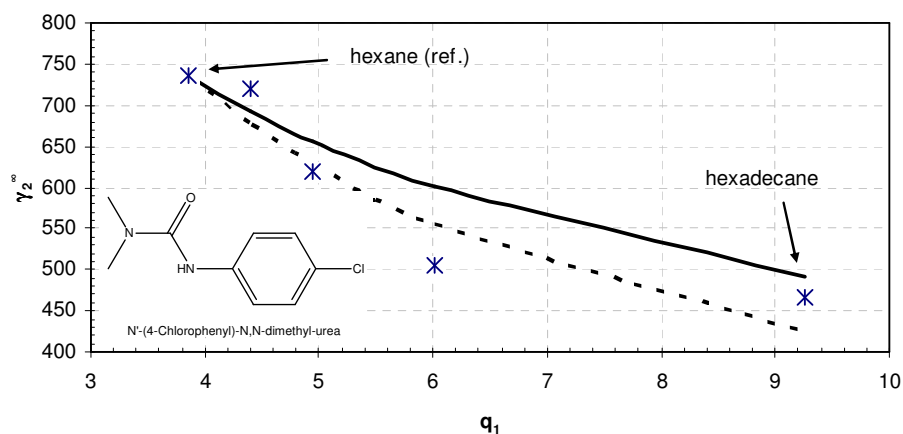


Figure 4: γ_2^∞ vs. q_1 for N'-(4-chlorophenyl)-N,N-dimethyl-urea (2) in alkane solvents(1) using hexane as the reference solvent at 298.15 K (x – data from the DDB (Gmehling et al. 2008), — Eqn.(3), --- Eqn.(5)).

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 affected 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.

Conclusion

A method has been developed which enables the infinite dilution activity coefficient in one alkane solvent to be transformed to any other alkane solvent with knowledge of the molar volumes and van der Waals volumes and surface areas. Another application of this method is the development of new combinatorial expressions similar to the one developed in this work.

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