

# PREDICTION OF DIFFUSIVITIES IN LIQUID ASSOCIATING SYSTEMS ON THE BASIS OF A MULTICOMPONENT APPROACH

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## ABSTRACT

A model for the prediction of pseudo-binary Maxwell-Stefan diffusivities in binary systems with association and solvation effects has been developed. In analogy to the chemical theory this model is based on a multicomponent approach for the Maxwell-Stefan diffusion coefficients. To reduce the number of multicomponent diffusivities a correlation factor has been developed depending on the mole fractions and the acentric factor. The reaction equilibrium constants for the association and solvation reaction have been computed from the UNIQUAC association model. For first model assessment the results obtained from this approach are compared with experimental findings for the system ethanol-cyclohexane gathered from Taylor dispersion experiments. This comparison reveals an accurate description of the diffusivities in the diluted regions whereas larger deviations are to be expected in the middle concentration range. These deviations can be explained with the shape of the thermodynamic correction factor computed from  $g^E$ -models where their influence on the prediction accuracy of diffusion coefficients has been additionally examined. It can be shown that the UNIQUAC association model is superior to the Wilson equation in describing the VLE data of the system investigated, especially in the diluted concentration ranges. From this it can be concluded that the correction factor computed with this model yields diffusivities of higher accuracy for this type of system.

## INTRODUCTION

Diffusion plays an important role in all kinds of separation processes, e.g. distillation or absorption. Since the increasing usage of nonequilibrium (NEQ) stage modelling [1] a deeper insight into mass transfer has become more important in order to allow accurate and reliable predictions of e.g. concentration profiles in any kind of equipment. Fundamental knowledge on various physical and thermodynamic properties, e.g. diffusion coefficients, is required. Especially in highly non-ideal systems, thermodynamic non-idealities – caused by different sizes, shapes, and interaction energies as well as association and solvation of molecules – strongly

influence the diffusional behaviour. Even for binary systems these effects usually result in large deviations between experimental data and predicted values since neither the Maxwell-Stefan-diffusivity models (MS) nor the  $g^E$ -models commonly used, e.g. UNIQUAC or Wilson, account for chemical interactions.

Diffusion problems are tackled with the Fick's law or the Maxwell-Stefan equation. The relation between the two has been given by Taylor and Krishna [2]. For a binary mixture this yields:

$$D = \Gamma \mathcal{D} \quad (1)$$

As can be seen from this equation the Fick diffusivity,  $D$ , equals the MS diffusion coefficient,  $\mathcal{D}$ , times the thermodynamic correction factor,  $\Gamma$ . The main difference between both models is that the MS-approach separates diffusional effects from thermodynamic non-idealities while the Fick diffusion coefficients must also account for the non-idealities in the mixture.

Several investigators have attempted to develop models to predict diffusivities. Satisfactory results can be obtained for ideal and slightly non-ideal binary mixtures whereas these approaches fail for highly non-ideal systems, e.g. systems with an alcohol or ketone as solute. At first sight, only two constituents are present in such mixtures, namely the monomer molecules of a solute ( $A$ ), e.g. alcohol, and a solvent ( $B$ ). In reality these mixtures consist of several components due to association and solvation effects between the various species formed. Therefore, it is straightforward to model such systems in terms of a multicomponent approach. A first attempt was conducted by Mc Keigue and Gulari [3] who predicted Fick diffusivities. Later, another attempt has been made by Rutten [4] who developed a model to predict MS-diffusivities in an associating system, where only solute-solute interaction effects are considered. A different model was also derived by him that describes the situation of a solvating system in which only  $A$ ,  $B$  and the solvated species  $AB$  are present.

The multicomponent models derived are only of limited use since in most systems solute-solvent interaction effects do also occur. Therefore, the main goal of this work is to present a model that accounts for both effects simultaneously. Due to the separate treatment of non-idealities and the diffusional process itself, the MS-diffusivity approach is preferred throughout this work. Based on Rutten's ideas his association model has been further developed to account also for solvating effects. Additionally, the reaction equilibrium constants required for the association and solvation reactions will be computed from an extension of the commonly used UNIQUAC model which also accounts for these effects.

The present work is outlined as follows. First, the derivation of the MS-diffusivity model is given followed by a brief introduction to the UNIQUAC association model. In order to validate the proposed diffusivity model the computed diffusion coefficients will be compared with experimental data for the binary system ethanol-cyclohexane obtained from a Taylor dispersion unit. Since the  $g^E$ -model chosen plays a decisive role in the prediction of Fick diffusivities the thermodynamic correction factor will also be computed from the Wilson equation and the results compared with the ones obtained from the UNIFAC association model.

## THEORY

### Theoretical Derivation of the MS-Diffusivity Model

Diffusion processes in binary systems with association and solvation effects can be treated in two ways. From a macroscopic point of view the mass transfer in such a system can be described in terms of the monomer species  $A$  (solute) and  $B$  (solvent) which form this binary mixture. In contrast, it can also be characterised as a multicomponent mixture regarding associates and solvates formed by H-bondings as distinct chemical species. Since both points of view describe the same chemical system the findings obtained from the two approaches must be equal. This is a prerequisite for the model derivation below.

The theoretical part is divided as follows. First, the mass transfer in the multicomponent mixture will be derived, afterwards the same mixture will be treated as a pseudo-binary system. Finally, both mass transfer relations will be equated to deduce the pseudo-binary MS-diffusivity as a function of the multicomponent MS-diffusivities.

### Modelling of the system as a multicomponent mixture

As mentioned in the introductory part of this work a mixture consisting of associated or solvated species can be regarded as a multicomponent mixture. The reactions taking place to form associates and solvates are considered as equilibrium reactions whereas association and solvation must be treated separately.

*Association:*

$$A + A_{i-1} \rightleftharpoons A_i$$
$$K_i^A = \frac{\gamma_{A_i} x_{A_i}}{(\gamma_A x_A)(\gamma_{A_{i-1}} x_{A_{i-1}})} \quad (2)$$

*Solvation:*

$$A_i + B \rightleftharpoons A_i B$$
$$K_i^S = \frac{\gamma_{A_i B} x_{A_i B}}{(\gamma_{A_i} x_{A_i})(\gamma_B x_B)} \quad (3)$$

From these equations it can be seen that  $2n - 1$  chemical species are present in the mixture:

- $n - 1$  associates (incl. monomer  $A$ ), i.e.  $A, A_2, \dots, A_{n-1}$
- $n - 1$  solvates, i.e.  $AB, A_2B, \dots, A_{n-1}B$
- 1 monomer  $B$

Here,  $n$  describes the number of associates formed including the two monomer components, e.g.  $n = 3 \Rightarrow A, A_2, B$ . For the model derivation the mole fractions of these components are ordered as follows:

$$x_1 = A, x_2 = A_2, \dots, x_{n-1} = A_{n-1}, x_n = AB, \dots, x_{2n-2} = A_{n-1}B, x_{2n-1} = B$$

The same indices apply to other variables, too.

### **Diffusional fluxes in the multicomponent system**

The diffusion fluxes of the various species can be easily written in terms of the Maxwell-Stefan-equations. Hence, the fluxes of  $2n-2$  components are given by:

$$\dot{n}_i = -c_t \sum_{j=1}^{2n-2} A_{ij} d_j = -c_t \sum_{j=1}^{n-1} A_{ij} d_j - c_t \delta \sum_{j=n}^{2n-2} A_{ij} d_j \quad (4)$$

whereas  $A_{ij}$  is an element of the inverse matrix of  $[B]$  with dimension  $(2n-2)$  and  $d_j$  equals the driving force of  $j$ . The elements of matrix  $[B]$  are defined according to the derivation of the MS-model [2].

$$B_{ii} = \frac{x_i}{D_{in}} + \sum_{\substack{k=1 \\ k \neq i}}^{2n-1} \frac{x_k}{D_{ik}} \quad (5)$$

$$B_{ij} = -x_i \left( \frac{1}{D_{ij}} - \frac{1}{D_{in}} \right) \quad (6)$$

The additionally introduced variable  $\delta$  in (4) denotes solvation effects. For  $\delta=1$  solvation effects occur, if  $\delta=0$  only association effects are considered and the equations can be simplified. The flux of the last constituent ( $2n-1$ ) is defined with respect to the bootstrap relation

$$\sum_{i=1}^{2n-1} \dot{n}_i = 0$$

to give:

$$\dot{n}_{2n-1} = -\sum_{i=1}^{2n-2} \dot{n}_i = c_t \sum_{i=1}^{2n-2} \sum_{j=1}^{2n-2} A_{ij} d_j \quad (7)$$

### **Driving forces**

Due to the Gibbs-Duhem restriction only  $2n-2$  driving forces are independent:

$$\sum_{i=1}^{2n-1} d_i = \sum_{i=1}^{2n-1} x_i f_i = \sum_{i=1}^{n-1} x_i f_i + x_{2n-1} f_{2n-1} + \delta \sum_{i=n}^{2n-2} x_i f_i = 0 \quad (8)$$

The dimensionless driving force  $f_i$  is defined by:

$$f_i = \frac{1}{RT} \nabla \mu_i = \frac{1}{RT} \nabla \ln(\gamma_i x_i) \quad (9)$$

Combining these equations with the equilibrium reactions gives relations between the various driving forces of the species formed and those of the monomers. Here must also the two cases be discerned.

*Association* ( $i=1 \dots n-1$ ):

The driving force on the associated species can easily be derived in terms of the driving force on the monomer species  $A$ . From (2) and (9) the following equation can be obtained

$$f_i = f_1 + f_{i-1}$$

or

$$f_i = i f_1 \quad (10)$$

which results in:

$$d_i = \frac{i x_i}{x_1} d_1 \quad (11)$$

*Solvation* ( $i = n \dots 2n - 2$ ):

The same can be applied to the second set of reaction equations which finally results in:

$$f_i = f_{i-n+1} + f_{2n-1}$$

Together with (10) the relation can be rewritten to give

$$f_i = (i - n + 1)f_1 + f_{2n-1} \quad (12)$$

or:

$$d_i = x_i \left( \frac{(i - n + 1)d_1}{x_1} + \frac{d_{2n-1}}{x_{2n-1}} \right) \quad (13)$$

Combining the relations derived thus far yields an expression for the driving forces of the monomer species in the multicomponent mixture, i.e. insertion of (10) and (12) in (8) gives

$$f_{2n-1} = - \frac{\sum_{i=1}^{n-1} i x_i + \delta \sum_{i=n}^{2n-2} (i - n + 1) x_i}{x_{2n-1} + \delta \sum_{i=n}^{2n-2} x_i} f_1 \quad (14)$$

or:

$$\begin{aligned} d_{2n-1} &= - \frac{\sum_{i=1}^{n-1} i x_i + \delta \sum_{i=n}^{2n-2} (i - n + 1) x_i}{x_{2n-1} + \delta \sum_{i=n}^{2n-2} x_i} \frac{x_{2n-1}}{x_1} d_1 \\ &= \alpha \frac{x_{2n-1}}{x_1} d_1 \end{aligned} \quad (15)$$

### **Modelling of the system as a 'pseudo'-binary mixture**

Now the same amount of mixture is considered as a pseudo-binary, in which solely the monomer species  $A$  and  $B$  occur. In order to distinguish between pseudo-binary and multicomponent variables, capital letters are used to denote the former case.

#### ***Diffusion flux in the 'pseudo' binary mixture***

Setting up the MS-equation for total  $A$  yields:

$$-C_T \mathcal{D}D_1 = X_{2n-1} \dot{N}_1 - X_1 \dot{N}_{2n-1} \quad (16)$$

The indices used have been adopted from the derivation of the multicomponent system.

#### **Relation between both descriptions**

As aforementioned the goal is to find a relation between the two different approaches, i.e. to express the pseudo-binary diffusivity in terms of the multicomponent MS-diffusivities which are hidden in the matrix  $[A]$ .

In order to relate the two approaches the variables, i.e. mole fractions, driving forces, and diffusivities, of the pseudo-binary model must be expressed as functions of the multicomponent variables.

#### ***Mole fractions***

First, the real (multicomponent) mole fractions are related to the overall (pseudo-binary) mole fractions of  $A$  and  $B$  in the following way

$$X_1 = \frac{N_1}{N_1 + N_{2n-1}}$$

with the pseudo-number of moles  $N_1$  and  $N_{2n-1}$  defined by:

$$\begin{aligned} N_1 &= \sum_{i=1}^{n-1} i n_i + \delta \sum_{i=n}^{2n-2} (i-n+1) n_i \\ N_{2n-1} &= n_{2n-1} + \delta \sum_{i=n}^{2n-2} n_i \end{aligned} \quad (17)$$

From these equations the relation between the mole fractions can be deduced:

$$X_1 = \frac{\sum_{i=1}^{n-1} i x_i + \delta \sum_{i=n}^{2n-2} (i-n+1) x_i}{\sum_{i=1}^{n-1} i x_i + x_{2n-1} + \delta \left( \sum_{i=n}^{2n-2} (i-n+1) x_i + \sum_{i=n}^{2n-2} x_i \right)} \quad (18)$$

$$X_{2n-1} = \frac{x_{2n-1} + \delta \sum_{i=n}^{2n-2} x_i}{\sum_{i=1}^{n-1} i x_i + x_{2n-1} + \delta \left( \sum_{i=n}^{2n-2} (i-n+1) x_i + \sum_{i=n}^{2n-2} x_i \right)} \quad (19)$$

### Driving forces

Compared to the multicomponent mixture the number of moles in the pseudo-binary system is larger by a factor  $r$ .

$$r = 1 + \sum_{i=1}^{n-1} (i-1) x_i + \delta \sum_{i=n}^{2n-2} (i-n) x_i$$

With this, the driving forces of the two systems are linked as follows:

$$r X_1 F_1 = \left( \sum_{i=1}^{n-1} i x_i + \delta \sum_{i=n}^{2n-2} (i-n+1) x_i \right) f_1 \quad (20)$$

Introducing the definition of  $r$  and (18) in (20) yields the following expression for monomer species  $A$ :

$$F_1 = f_1 \quad (21)$$

The same is true for component  $B$ :

$$F_{2n-1} = f_{2n-1} \quad (22)$$

### Pseudo-binary diffusivity

On the basis of the equations derived the relation between the pseudo-binary and the multicomponent diffusivities can be deduced. Starting point is (16) whose variables are consecutively substituted. In the following the derivation is given step by step, starting with the right-hand side of this equation. Combining with an analogous definition to (17) for fluxes and (7) yields:

$$\begin{aligned} r \left( X_{2n-1} \dot{N}_1 - X_1 \dot{N}_{2n-1} \right) &= r \left[ X_{2n-1} \left( \sum_{i=1}^{n-1} i \dot{n}_i + \delta \sum_{i=n}^{2n-2} (i-n+1) \dot{n}_i \right) - X_1 \sum_{i=n}^{2n-1} \dot{n}_i \right] \\ &= r \left[ X_{2n-1} \left( \sum_{i=1}^{n-1} i \dot{n}_i + \delta \sum_{i=n}^{2n-2} (i-n+1) \dot{n}_i \right) + X_1 \sum_{i=1}^{n-1} \dot{n}_i \right] \end{aligned} \quad (23)$$

With (4):

$$= -c_i r \left[ \begin{aligned} &\sum_{i=1}^{n-1} (X_{2n-1} i + X_1) \left( \sum_{j=1}^{n-1} A_{ij} d_j + \delta \sum_{j=n}^{2n-2} A_{ij} d_j \right) \\ &+ X_{2n-1} \delta \sum_{i=n}^{2n-2} (i-n+1) \left( \sum_{j=1}^{n-1} A_{ij} d_j + \sum_{j=n}^{2n-2} A_{ij} d_j \right) \end{aligned} \right] \quad (24)$$

Before continuing with the insertion of new terms, the summation terms over  $j$  are derived first. The driving forces are related to the driving forces of the monomer species by introducing (11) and (13) and afterwards (15):

$$\begin{aligned}
\sum_{j=1}^{n-1} A_{ij} d_j + \delta \sum_{j=n}^{2n-2} A_{ij} d_j &= \sum_{j=1}^{n-1} j A_{ij} \frac{x_j}{x_1} d_1 + \delta \sum_{j=n}^{2n-2} A_{ij} x_j \left( \frac{j-n+1}{x_1} d_1 + \frac{d_{2n-1}}{x_{2n-1}} \right) \\
&= \sum_{j=1}^{n-1} j A_{ij} \frac{x_j}{x_1} d_1 + \delta \sum_{j=n}^{2n-2} A_{ij} x_j \left( \frac{j-n+1}{x_1} d_1 + \frac{\alpha}{x_1} d_1 \right) \\
&= \frac{d_1}{x_1} \left[ \sum_{j=1}^{n-1} j A_{ij} x_j + \delta \sum_{j=n}^{2n-2} A_{ij} x_j (j-n+1+\alpha) \right] \\
&= \frac{d_1}{x_1} \beta
\end{aligned} \tag{25}$$

With (25) introduced in (24) the right-hand side can be written as:

$$= -c_i r \frac{d_1}{x_1} \left[ \sum_{i=1}^{n-1} (X_{2n-1} i + X_1) \beta + X_{2n-1} \delta \sum_{i=n}^{2n-2} (i-n+1) \beta \right] \tag{26}$$

By defining

$$x_{sum} = \sum_{i=1}^{n-1} i x_i + \delta \sum_{i=n}^{2n-2} (i-n+1) x_i \tag{27}$$

and making use of (18) and (19) the following expression can be obtained for the right-hand side of (16):

$$= -c_i r \frac{d_1}{x_1} \left[ \sum_{i=1}^{n-1} \frac{i(x_{2n-1} + \delta \sum_{k=n}^{2n-2} x_k) + x_{sum}}{x_{sum} + x_{2n-1} + \delta \sum_{k=n}^{2n-2} x_k} \beta + \delta \frac{\sum_{k=n}^{2n-1} x_k}{x_{sum} + \sum_{k=n}^{2n-1} x_k} (i-n+1) \beta \right] \tag{28}$$

The left-hand side of (16) is easier to develop. First, the pseudo-binary driving force  $D_1$  can be substituted by the dimensionless one:

$$-r C_T D D_1 = -C_T D r X_1 F_1 \tag{29}$$

Using (20) leads to:

$$\begin{aligned}
&= -C_T D \left( \sum_{i=1}^{n-1} i x_i + \delta \sum_{i=n}^{2n-2} (i-n+1) x_i \right) f_1 \\
&= -C_T D \frac{x_{sum}}{x_1} d_1
\end{aligned} \tag{30}$$

With  $r = C_T / c_i$  both sides can be linked again and the expression for the pseudo-binary MS-diffusivity can finally be written

$$D = \frac{1}{x_{sum}} \left[ \begin{aligned} &\sum_{i=1}^{n-1} \frac{i x_{2n-1} + x_{sum} + \delta i \sum_{k=n}^{2n-2} x_k}{x_{sum} + x_{2n-1} + \delta \sum_{k=n}^{2n-2} x_k} \beta \\ &+ \delta \frac{\sum_{k=n}^{2n-1} x_k}{x_{sum} + \sum_{k=n}^{2n-1} x_k} \sum_{i=n}^{2n-2} (i-n+1) \beta \end{aligned} \right] \tag{31}$$

whereas  $\beta$  is then defined by:

$$\beta = \left[ \sum_{j=1}^{n-1} j A_{ij} x_j + \delta \sum_{j=n}^{2n-2} A_{ij} x_j (j - n + 1 + \alpha) \right]$$

$\alpha$  can be written in a similar way:

$$\alpha = - \frac{x_{sum}}{x_{2n-1} + \delta \sum_{i=n}^{2n-2} x_i}$$

The model derived here incorporates both multicomponent models derived by Rutten. For  $\delta = 0$  and  $n > 2$  the association model is obtained while for  $\delta = 1$  with  $n = 2$  the solvation model can be found.

In respect to a first model validation presented below the derivation of the diffusivities at infinite dilution will be given for the case of an associating system, i.e.  $\delta = 0$ . Then, (31) reduces to the following expressions in which the left hand sides can be either determined from experimental diffusivity data at infinite dilution or from an appropriate model, e.g. Wilke-Chang [5]:

$$X_1 \rightarrow 0 \quad D = D_{1,2n-1} = D_{AB} \quad (32)$$

$$X_{2n-1} \rightarrow 0 \quad D = \left[ \sum_{i=1}^{n-1} \frac{x_i}{D_{i,2n-1}} \right]^{-1} \quad (33)$$

Following Rutten's derivation values for the multicomponent diffusivities of the associated and solvated species have been estimated by relating them to the multicomponent diffusivity of the monomers using a "correlation factor",  $C_{ij}$ .

$$D_{i,j} = C_{i,j} D_{1,2n-1} \quad (34)$$

For these constants he chose a ratio of the van der Waals radii:

$$C_{ij} = \frac{R_{vdW,1} R_{vdW,2n-1}}{R_{vdW,i} R_{vdW,j}} \quad (35)$$

The van der Waals radius in turn is defined by

$$R_{vdW} = \left( \frac{3V_{vdW}}{4\pi N_A} \right)^{1/3} \quad (36)$$

whereas the van der Waals volumes,  $V_{vdW}$ , of the associates are taken as multiples of the volume of the monomer solute. Values for the van der Waals volumes have been listed by Edward [6] and Bondi [7]. As will be shown later this type of diffusivity relation can be further improved to allow predictions with higher accuracy.

The monomer pair diffusivity may now be computed as follows. (32) yields the diffusivity at infinite dilution in pure solvent which is equal to the binary experimental value. In order to obtain the infinite dilution diffusivity in pure solute (33)-(35) must be combined which yields a value depending on the mixture composition, i.e. equilibrium constants. At intermediate composition the multicomponent diffusion coefficient of the monomer pair is computed from the infinite dilution diffusivities using a mixing rule, e.g. Vignes [8]. Once these diffusivities have been calculated the computation of the binary diffusivity given in (31) is straightforward.



### **The UNIQUAC Association Model**

In 1999 Asprion has extended the commonly used UNIFAC model to account also for association effects [9]. In his work binary and ternary mixtures of alcohols in both inert and solvating solvents were investigated by spectroscopic analysis in respect to the structure of the associates and solvates formed. In addition to the structure analysis, phase equilibrium measurements were conducted in order to obtain new sets of interaction parameters. In the resulting UNIQUAC association model the molecular species are introduced as groups, similar to the commonly used UNIQUAC model. In the following the derivation of this model with respect to systems in which only association reactions occur, i.e. an alcohol as solute in an inert solvent, will be presented.

In this model are associates regarded as separate chemical species with reaction equilibria defined by (2). The required equilibrium constants were determined from independent FT-IR measurements. For correlation purposes the number of associates considered in the model was reduced by assuming that, besides dimer association, only one higher associated species had been formed. This higher oligomer can be seen as a representative for all higher associates occurring in the mixture. For the calculation of the equilibrium constant the following relation is favoured

$$\ln K_k = -\frac{\Delta_R h_k^{\text{Ref.}}}{RT} + \frac{\Delta_R S_k^{\text{Ref.}}}{R} \quad k = Di, Po \quad (37)$$

whereas the reaction enthalpy and reaction entropy for the dimer reaction are given by:

$$\Delta_R h_{Di}^{\text{Ref.}} = \frac{\Delta_R h_{Po}^{\text{Ref.}}}{n-1} - \Delta h_{Di} \quad (38)$$

$$\Delta_R S_{Di}^{\text{Ref.}} = \frac{\Delta_R S_{Po}^{\text{Ref.}}}{n-1} - \Delta S_{Di} \quad (39)$$

Here,  $n$  refers to the number of solute molecules in an associate. The values for the dimer reaction enthalpy and entropy for the alcohol–inert solvent systems investigated are as follows:

$$\Delta h_{Di} = -12.023 \text{ kJ/mol} \quad (40)$$

$$\Delta S_{Di} = -30.031 \text{ J/(mol K)} \quad (41)$$

Example values for the reaction enthalpy and reaction entropy, which are assumed to be independent of temperature and pressure, of higher oligomers can be found in Table 1.

Table 1: Reaction enthalpies and entropies for solvents *n*-hexane and cyclohexane

Component	<i>n</i>	$-\frac{\Delta_R h_{Po}^{Ref.}}{n-1}$ [kJ/mol]	$-\frac{\Delta_R S_{Po}^{Ref.}}{n-1}$ [J/(mol K)]
Methanol	5	27.524	51.174
Ethanol	5	27.524	54.162
1-Propanol	5	27.524	56.690

Since the UNIQUAC association model does not distinguish between the interaction of alcohol groups in a monomer and in an oligomer with a solvent molecule, only two interaction parameters are needed per binary system.

Table 2: Interaction parameters for ethanol in cyclohexane

$a_{12}/K$	$a_{21}/K$
-35.719	121.78

On the basis of this information it is possible to compute multicomponent activity coefficients and also the thermodynamic correction factor. Additionally, the species distribution crucial for the diffusivity model is also obtained.

## EXPERIMENTS

In order to validate the model diffusion coefficients have been experimentally determined in a Taylor dispersion unit. The experimental set-up of this unit consists of standard HPLC-equipment which has been fully automated (see Figure 1). All experiments have been conducted isothermally at 25°C.

The chemicals obtained from Merck Eurolab GmbH were of analytical grade and used without further purification.

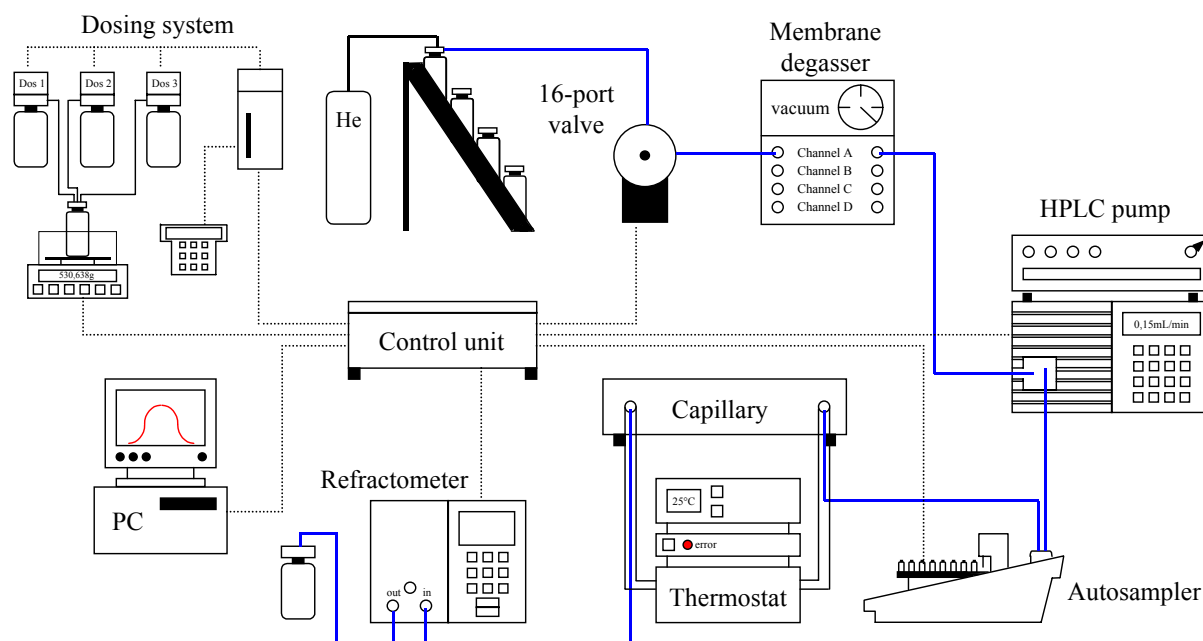


Figure 1: Experimental set-up of the Taylor dispersion unit

## RESULTS

In order to validate the model proposed here experimental data on diffusivities have been acquired from Taylor dispersion experiments. Validation experiments of the apparatus have been conducted for the systems methanol-water and ethanol-water. The deviation of the experimental findings from literature data are within 2% which equals the accuracy known for this type of apparatus. A new set of diffusivity data is given in Table 3 for the binary system ethanol-cyclohexane measured at 25°C.

Table 3: Diffusivity data for the system ethanol (1) – cyclohexane (2)

$x_1$	3%	10%	20%	30%	40%	50%	60%	70%	80%	90%	97%
$D_{12}$ [m <sup>2</sup> /s 10 <sup>9</sup> ]	0.991	0.767	0.520	0.425	0.423	0.465	0.574	0.730	0.950	1.232	1.411

The diffusivities at infinite dilution have been determined from extrapolation of the data by fitting a polynomial of degree five (correlation factor = 99.9%).

$$D_{12}^0 = 1.138 \cdot 10^{-9} \text{ m}^2 / \text{s} \quad D_{21}^0 = 1.500 \cdot 10^{-9} \text{ m}^2 / \text{s}$$

As mentioned in the introduction a thermodynamic correction factor interrelates the Fick and the MS-diffusivities and has, therefore, a great impact on the outcome of the modelling process. Hence, it is worthwhile to compare the prediction of the UNIQUAC association model with the Wilson equation known to be as one of the most accurate models in predicting VLE data. Recommended VLE data have been taken from the DECHEMA data series [10] for the above mentioned system together with the corresponding interaction parameters given for the Wilson equation. Figure 2 depicts the activity coefficients computed from the experimental data and the predictions of both models. It is obvious that both models are capable of describing the data in the region researchers are mostly interested in, i.e. the middle concentration range, whereas larger differences can be seen in the highly diluted concentration ranges. For ethanol infinitely diluted in cyclohexane the Wilson equation predicts an activity coefficient noticeably smaller than the UNIQUAC association model does. The reason for this can be seen in the additional consideration of chemical interaction effects in the UNIQUAC association model which are remarkable in this concentration range. Comparison with literature data on activity coefficients at infinite dilution [11, 12] reveals that the prediction of the UNIQUAC association model is close to the values reported. The consequences become obvious in the different predictions of the thermodynamic correction factor as depicted in Figure 3. Especially in the diluted regions deviations between the models are apparent which ultimately result in different findings for the diffusion coefficients. Summarising, it can be presumed that computing the thermodynamic correction factor with the UNIQUAC association model yields diffusivities of higher accuracy for this system than with the Wilson equation. Nevertheless, both models have been used to compute MS-diffusivities from the experimental data to reveal the influence of the  $g^E$ -model on this transport property.

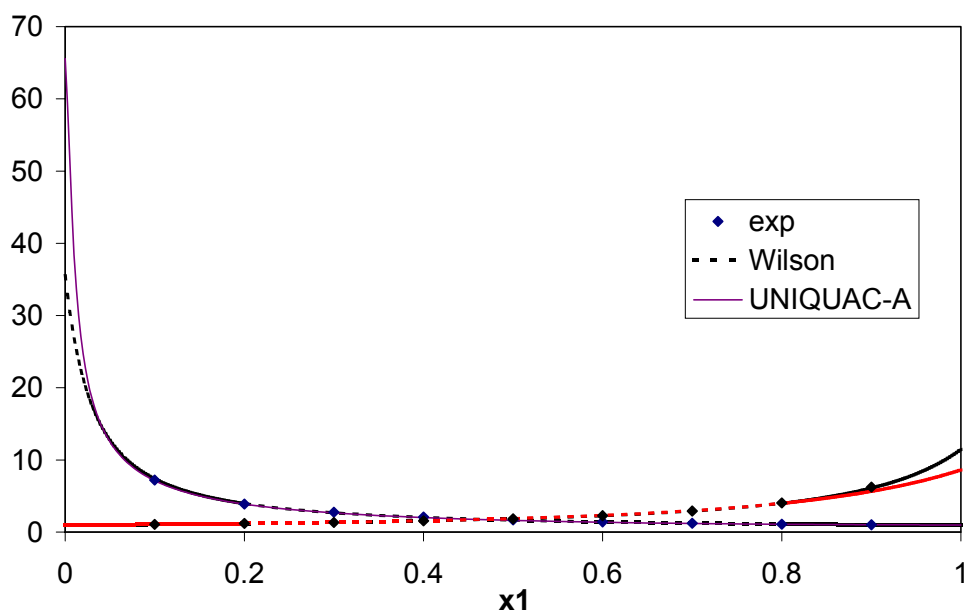


Figure 2: Activity coefficients for an ethanol-cyclohexane mixture computed with the Wilson equation and the UNIQUAC association model

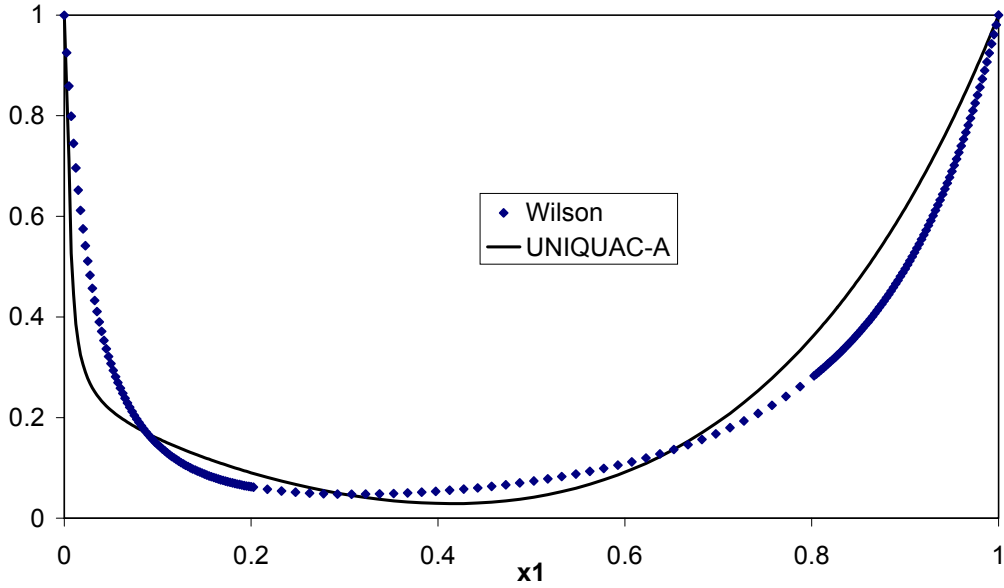


Figure 3: Thermodynamic correction factors for Wilson and the UNIQUAC association model

As Rutten found out [13] relating the various MS-diffusivities of the associates and solvates to the one of the monomer species in the multicomponent mixture by means of van der Waals radii yields an incorrect volume correction in the diluted solute region. Therefore, several methods have been tried to find a new expression for the correlation factors  $C_{ij}$  which takes both the concentration dependence and the non-roundness, i.e. deviation from a sphere, into account. For this purpose the volume fraction as defined in the UNIQUAC equation

$$\phi_i = \frac{r_i}{\sum_{j=1}^{2n-1} x_j r_j} \quad (42)$$

and the acentric factor computed from the Lee-Kesler method [14] combined with the Joback method [15] for critical properties have been related to each other in various ways. The resulting correlation factors are given by the ratios of the various combinations, e.g. model 1b of the following tables:

Table 4: Correlation factors and sum of least squares with Wilson

	$\frac{\phi_i}{\omega_i}$	$\frac{\phi_i^{x_i}}{\omega_i}$	$\frac{R_{vdW,i}}{\omega_i}$	$\frac{(1/\phi_i)}{\omega_i}$	$\frac{(1/\phi_i)^{x_i}}{\omega_i}$	$\frac{1/R_{vdW,i}}{\omega_i}$
Model/ac. factor	W1	W2	W3	W4	W5	W6
$\omega_i = 1$ (a)	2526	579	1157	17842	446	728
$\omega_i = \text{var.}$ (b)	1246	3391	607	175036	3799	1094
$1/(\omega_i = \text{var.})$ (c)	3328	1899	2459	799	1754	15794

$$C_{ij} = \frac{\left(\frac{\phi_1}{\omega_1}\right)\left(\frac{\phi_{2n-1}}{\omega_{2n-1}}\right)}{\left(\frac{\phi_i}{\omega_i}\right)\left(\frac{\phi_j}{\omega_j}\right)} \quad (43)$$

Tables 4 and 5 show all the combinations used together with the resulting sums of least squares when applying either of the  $g^E$ -models.

The tables reveal that for both  $g^E$ -models the model 5a performs best. However, larger deviations are to be expected. In Figure 4 a comparison is given for the MS-diffusivities computed from experimental data and the predicted values calculated with the best performing correlation factors and the Wilson equation. It is obvious that neither method can adequately represent the source data. By variation of the acentric factor it is possible to greatly improve the prediction accuracy in the concentration range  $x_1 > 0.3$  which comes at the expense of larger inaccuracies in the diluted alcohol regions (curve is then similar to W4c). A similar picture can be drawn for the UNIQUAC association model. The correlation factors used can picture only qualitatively the curve computed from experimental data.

The influence of these inaccuracies on the prediction of the Fick diffusion coefficients is depicted in Figure 5. Here, the experimentally determined data as well as the predicted values computed with the correlation factors performing best are presented. Additionally, values calculated in accordance with Rutten's model are given for comparison purposes. Due to the overprediction of the MS-diffusivities in the diluted region (Wilson equation) the experimental data cannot be properly reflected, see curve W5a. Comparison of this curve with Rutten's model (W3a, not shown) shows that with the modified correlation factor predictions of higher accuracy can be made. As previously mentioned variation of the acentric factor yields high resemblance for the predicted values and the Fick data whereas the deviation in the diluted region increases markedly. In contrast, the values computed from the UNIQUAC association model perform better in the diluted region while deficiencies in the middle concentration range occur. Again, varying the acentric factor results in better agreement to the experimental data. Comparing U2a with U3a (Rutten) shows that the correlation factor used for U2a is superior to the ratio of the van der Waals

*Table 5: Correlation factors and sum of least squares with UNIQUAC association model*

	$\frac{\phi_i}{\omega_i}$	$\frac{\phi_i^{x_i}}{\omega_i}$	$\frac{R_{vdW,i}}{\omega_i}$	$\frac{(1/\phi_i)}{\omega_i}$	$\frac{(1/\phi_i)^{x_i}}{\omega_i}$	$\frac{1/R_{vdW,i}}{\omega_i}$
Model/ac. factor	U1	U2	U3	U4	U5	U6
$\omega_i = 1$ (a)	3062	1164	1703	18859	1014	1374
$\omega_i = \text{var.}$ (b)	1788	4169	1242	177089	4539	1643
$1/(\omega_i = \text{var.})$ (c)	3877	2435	2995	1455	2290	16780

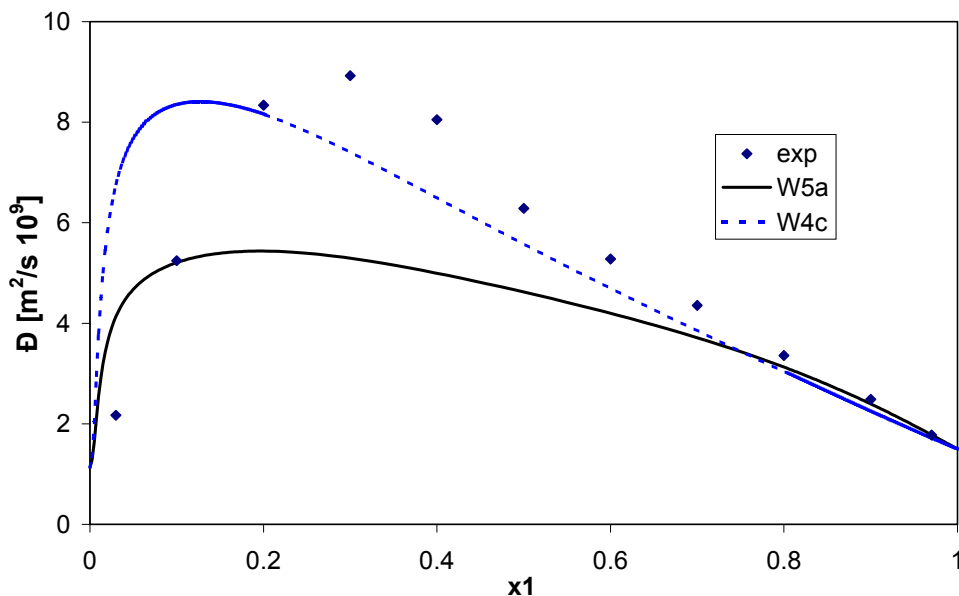


Figure 4: MS-diffusivities predicted from the Wilson equation

radii. In Table 6 the sums of least squares are given for the models presented in the last Figure. The results clearly demonstrate that the model performing best is U2a.

Table 6: Sums of least squares for Fick diffusivities computed with both  $g^E$ -models

	2a	3a (Rutten)	5a
Wilson	20	11	16
UNIQUAC assoc	2	8	5

## CONCLUSIONS

In this work a new model for the prediction of diffusivities in binary liquid systems in which association and solvation effects can occur has been presented. This model which is based on a previously developed association model by Rutten computes pseudo-binary MS-diffusivities from a multicomponent approach. The reaction equilibrium constants required for the computation of the association and solvation reaction equilibria have been adopted from the UNIQUAC association model. This  $g^E$ -model also serves to compute the thermodynamic correction factor, a proportionality constant that relates the Fick and the MS-diffusion coefficient.

Since this proportionality constant plays a decisive role in computing diffusivities the results for the thermodynamic correction factor obtained from the UNIQUAC association model and from the Wilson equation (recommended interaction parameters were used throughout this work) were compared. It could be shown that both models show excellent agreement with experimentally determined VLE data in the middle concentration range whereas the prediction of the Wilson equation fails at infinite dilution. In contrast, the UNIQUAC association model predicts this region also with high accuracy which ultimately results in differently shaped curves for the thermodynamic correction factor. This in turn affects the shape of the computed MS-diffusivity curves.

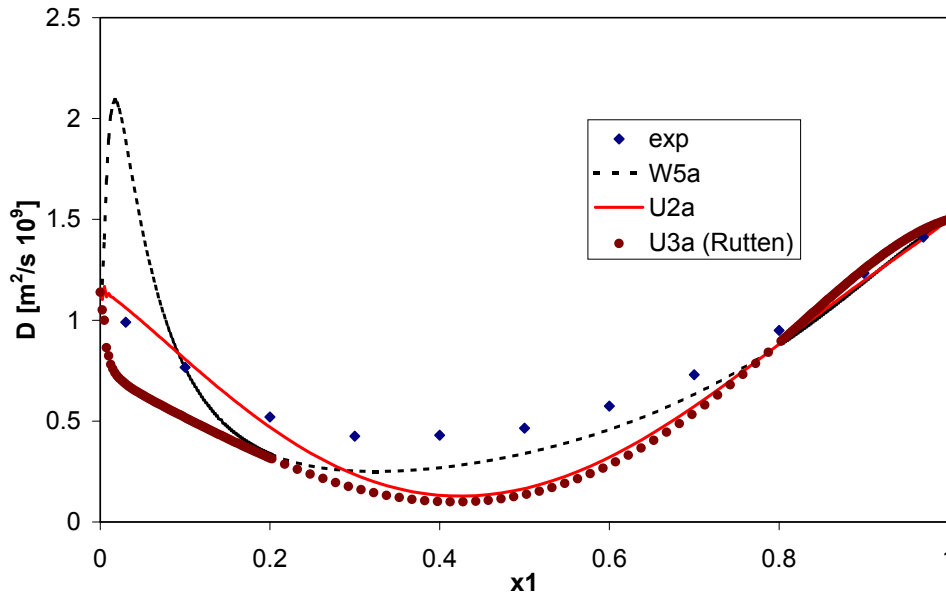


Figure 5: Comparison of experimental data and predicted values

These curves have been computed on the basis of a new set of experimental data determined for the binary system ethanol-cyclohexane from Taylor dispersion experiments ( $T=25^{\circ}\text{C}$ ). Validation of the experimental set-up showed that an relative error of 2% can be expected.

On the basis of this data a first assessment of the diffusivity approach proposed here has been conducted. Since the original correlation factor (a fixed ratio of van der Waals radii), used to decrease the number of MS-diffusivities in the multicomponent system, revealed erroneous volume corrections, this factor has been modified to account for the concentration dependence and the influence of non-roundness of the molecules. This has been done by using the volume ratio as defined in the UNIQUAC model and introducing the acentric factor computed from the Lee-Kesler method in conjunction with the Joback method for critical properties. Extensive testings revealed that the best performance (at least for this binary system) has been achieved with a modified correlation factor defined as  $C_{ij} = \phi_1^{x_i} \phi_{2n-1}^{x_{2n-1}} / (\phi_i^{x_i} \phi_j^{x_j})$  combined with the UNIQUAC association model. This resulted in good agreement with the experimental data in the diluted regions whereas larger deviations occurred in the middle concentration range. In contrast, the Wilson equation strongly overpredicted the diffusivities in the diluted regions which is caused by erroneous calculation of activity coefficients at infinite dilution. This also demonstrates clearly that the same set of interaction parameters applicable to VLE predictions does not necessarily yield accurate information on the second derivative of the  $g^E$ -model.

Further assessment of the proposed MS-diffusivity model is vital since only a special case, i.e. solely association reactions, has been investigated. In this way the modification of the correlation factor can be further tested. Investigation of the influence of  $g^E$ -models is also crucial in order to obtain reliable information on MS-diffusivities from experimental data.



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