Determination of Activities in Membrane Processes: The UNIQUAC Model Expressed in Mole and Mass Fractions

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DOI 10.1002/aic.12386

The universal quasi-chemical (UNIQUAC) model is widely used to describe nonideal fluid-phase equilibria in membrane processes. One way to overcome the problem of an unknown membrane molar mass, is to compute the membrane process performance in terms of mass fractions. Since molar and mass-based activity coefficients are not the same, the UNIQUAC equation is converted to mass-based expressions for correct simulation of membrane process performance. This conversion is described in view of general application for the description of mass transport through membranes. A validation of the conversion is performed successfully by calculating literature data by both versions of the UNIQUAC model, and comparing the results. Furthermore, potential applications of the theory are shown. Both liquid and vapor sorption isotherms are calculated. The results show good agreement between the theory described in this article and experimental results. © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 1889–1896, 2011
Keywords: UNIQUAC, mole/mass fractions, membrane process performance

Introduction

A significant part of chemical processes is concerned with separation of fluid mixtures by diffusional operations. Membrane processes can be a good alternative for these separations.[1] As membranes become more and more widely used in separation processes,[2,3] research aimed at modelling the process performance of membrane separations is of major interest. To simulate this performance correctly, a good transport model needs to be available.

Besides a thermodynamically correct transport description, more information is needed to compute the separation performance. All design methods for fluid mixture separations require quantitative estimates of fluid-phase equilibria. The excess Gibbs energy of a mixture gives information on the nonideal part of a mixture, as it gives the Gibbs energy of the solution in excess of what it would be if it were ideal. From a description of this excess Gibbs energy as a function of composition, activity coefficients can be calculated for mixtures.

The universal quasi-chemical (UNIQUAC) equation, as introduced by Abrams and Prausnitz in 1975[4] expresses this dependency. It is widely used to calculate activities and activity coefficients, not only for "liquid–liquid," but also for vapor-liquid equilibria. Since it only needs two adjustable parameters per binary pair and no ternary constants, it is a useful theory to describe the activity of multicomponent mixtures.

The original UNIQUAC equation describes the fluid-phase equilibrium in molar terms. However, a common problem in membrane technology is that the molar mass of the membrane is either unknown or a value cannot be assigned, and

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this value is often needed for simulation of the process performance in molar expressions. Different solutions for this problem have been reported in literature. Some considered an isothermal and isobaric binary membrane/solvent system, and assumed that the membrane molar concentration was negligible compared to that of the solvent.[5] Others tried to arbitrarily define values for the molar mass of the membrane, using repetitive segments as a measure for the macromolecular concentration.[6,7] Another modification often seen is the conversion to volume fractions for a multicomponent, isothermal, isobaric system.[8–11] However, all of these solutions have their own disadvantages.

A promising approach is to convert the equation to mass-based parameters. Since it is possible to measure the weight of a membrane, this overcomes the problem of unknown parameters in calculations. However, when looking at activity coefficients, the conversion is less straightforward. In molar-based expressions, the activity coefficient of an ideal liquid has a value of 1. However, in mass-based equations this no longer stands. The activities are the same for both expressions however. This is an important consequence of the conversion to mass fractions that cannot be overlooked during simulations.

This article reconsiders the UNIQUAC equation as presented by Abrams and Prausnitz[4] and describes the different parameters used in this expression. Next, the conversion to mass fractions will be stressed. To validate the conversion, activity coefficients are calculated with both molar- and mass-based approaches, and compared to literature data.

Finally, several test calculations are performed to predict fluid-membrane interactions. Both liquid and vapor sorption isotherms are calculated and compared to literature data, showing different potential applications of the theory for membrane performance predictions.

This approach has been reported before.[9,12,13] However, either errors have been found in the description of the converted UNIQUAC equation, or the definition of the converted equation requires a less precise method for determining the necessary parameters. These disadvantages are overcome in this research.

Theory

Deviations from ideal behavior (Raoult's law) are commonly expressed by activity coefficients. In a mixture, the activity coefficient γ_i (for component i) is related to g^E, the (average) excess Gibbs energy per mole of mixture, by:

$$n_t g^E = RT \sum_i n_i \ln \gamma_i \tag{1}$$

$$RT \ln \gamma_i = \left(\frac{\partial n_t g^E}{\partial n_i} \right)_{T,P,n_j(j \neq i)} \tag{2}$$

where n_i is the number of moles of component i and n_t the total number of moles. R, P, and T are the universal gas constant, pressure and temperature, respectively.

From the activity coefficient and the composition, the activity of a mixture can be calculated via

$$a_i = x_i \gamma_i \tag{3}$$

for molar-based parameters, or, when using mass-based parameters

$$a_i = w_i \gamma'_i \tag{3a}$$

In these equations a_i is the activity of the mixture, x_i is the molar fraction, w_i is the weight fraction, and γ_i and γ'_i are the molar-based and mass-based activity coefficients, respectively. These equations show there are two ways to calculate the activity, but the numerical value should be the same.

According to Eq. 2, activity coefficients can be obtained from an expression which gives g^E as a function of composition, pressure and temperature. For liquid mixtures at conventional pressures the effect of pressure is negligible. The effect of temperature is not negligible, but when considering a moderate temperature range it is often not large. This leaves composition as the most important parameter.

In the coming paragraphs, the original version of the UNIQUAC equation in terms of molar fraction composition is described, followed by the conversion to mass fractions as used in this article.

Universal quasi-chemical (UNIQUAC) equation

In 1975, Abrams and Prausnitz[4] introduced the UNIQUAC equation to describe the excess Gibbs energy of a mixture as a function of composition. This equation gives a good representation of both vapor-liquid and liquid–liquid equilibria for binary and multicomponent mixtures, while it only needs two adjustable parameters per binary pair. They also showed that this equation, if some well-defined simplifying assumptions are made, can yield any of several well-known expressions for the excess Gibbs energy, including the Van Laar, Wilson and NRTL equations.

The UNIQUAC equation accounts both for differences in size and shape and differences in energy of the different molecules in a mixture in respectively the combinatorial and the residual part of the equation. The total excess Gibbs energy can then be described as

$$g^E = g^E(\text{combinatorial}) + \mathrm{g^E}(\text{residual}) \tag{4}$$

The model uses different parameters to describe the structure of the molecules in the mixture. A liquid is represented by a three-dimensional lattice of equi-spaced lattice sites. Each molecule is divided into segments so that one segment occupies one cell in the lattice. If a molecule is represented by a set of bonded segments, the number of segments in molecule i is r_i. All segments have the same size per definition, but they differ in their external contact area. For molecule i, the number of external nearest neighbours is given by zq_i. Here, z is the average coordination number of the lattice, and q_i is a parameter proportional to the molecule's external surface area.

Using these parameters, for multicomponent mixtures, g^E (combinatorial) and g^E (residual) can be expressed as

$$\frac{g^E(\text{combinatorial})}{RT} = \sum_i x_i \ln \frac{\phi_i}{x_i} + \frac{z}{2} \sum_i q_i x_i \ln \frac{\theta_i}{\phi_i} \tag{5}$$

$$\frac{g^E(\text{residual})}{RT} = -\sum_i q_i x_i \ln \left(\sum_j \theta_j \tau_{ji} \right) \tag{6}$$

where

$$\tau_{ji} \equiv \exp -\left\{\left[\frac{u_{ji} - u_{ii}}{RT}\right]\right\} \tag{7}$$

and where the average area fraction θ and the average segment fraction ϕ are defined by

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \tag{8}$$

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \tag{9}$$

In these equations, x is the molar fraction of the component in the mixture. All summations are performed over all components, including component i.

θ is the average area fraction (dependent on the external surface parameter), and is therefore a surface parameter. ϕ is the average segment fraction (dependent on the number of segments) and is therefore a volume parameter. τ_{ji} is a binary interaction parameter and gives the fraction of external sites around molecule i occupied by molecule j. From Eq. 7 it follows that $\tau_{ii} = \tau_{jj} = 1$.

u_{ij} is an energy parameter and represents the average interaction energy of pairs of nonbonded segments between sites i and j. As can be seen, the combinatorial part of the UNIQUAC equation consists only of structural parameters, whereas the residual part also takes into account the energy difference between different molecules.

With the help of Eq. 2 the natural logarithm of the activity coefficient for component i can be determined by

$$\ln \gamma_i = \ln \gamma_i(\text{combinatorial}) + \ln \gamma_i(\text{residual}) \tag{10}$$

with

$$\ln \gamma_i(\text{combinatorial}) = \ln \frac{\phi_i}{x_i} + \left(\frac{z}{2}\right) q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \tag{11}$$

$$\ln \gamma_i(\text{residual}) = q_i \left(1 - \ln\left(\sum_j \theta_j \tau_{ji}\right) - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}}\right) \tag{12}$$

In these equations, l_i is determined from

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \tag{13}$$

To calculate the activity coefficients, the composition of the mixture and values for r_i, q_i, z, and τ_{ji} need to be known. r_i and q_i are pure component structural parameters and can be found in literature. Usually they are retrieved by group contribution methods, where the volume and surface parameters of the component are determined by the sum of these parameters of the different structural groups in the molecule (the segments).

Numerical results for ln γ_i are insensitive to the choice of coordination number z, provided a reasonable value ($6 \leq z \leq 12$) is assigned. However, adjustable parameters τ_{ij} and τ_{ji} depend on that choice. In this work, we have consistently used $z = 10$, just as Abrams and Prausnitz did. The binary interaction parameters τ_{ij} and τ_{ji} can then be found in literature or fit to experimental binary equilibrium data.

A modification of the original UNIQUAC equation was made to account for strong specific interactions by hydrogen bonding.[14] In this modification, the combinatorial part remains unchanged, and the residual part is extended with a term containing the parameter q_i^*, which is the effective surface of molecule i. It could be expected that only the residual part is changed, since hydrogen bonding mainly affects the energetic interactions.

q_i^* is a modified surface parameter related to pure component i. For nonassociating mixtures (no hydrogen bonding), q_i^* reduces to q_i. For mixtures that involve hydrogen bonding, q_i^* is inferior to q_i. This means that the surface of interaction q^* is smaller than the geometric external surface q, indicating that for these compounds intermolecular interaction is primarily determined by the OH-group, and thus accounting for the system contraction expected for molecules displaying strong specific interaction.

In the same way, θ_i^* is a modified volume fraction calculated on the basis of the modified surface parameter q_i* according to

$$\theta_i^* = \frac{q_i^* x_i}{\sum_j q_i^* x_j} \tag{14}$$

Since q_i^* is inferior to q_i, θ_i^* is also inferior to θ_i.

With these modifications, the residual part of the UNIQUAC equation becomes

$$\ln \gamma_i(\text{residual}) = q_i^* \left(1 - \ln\left(\sum_j \theta_j^* \tau_{ji}\right) - \sum_j \frac{\theta_j^* \tau_{ij}}{\sum_k \theta_k^* \tau_{kj}}\right) \tag{15}$$

As can be seen, this is equal to Eq. 12, except that q_i and θ_i are replaced by the newly defined parameters q_i^* and θ_i^*.

Conversion to mass fractions

To use the (extended) UNIQUAC equation for membrane processes where the process performance is simulated by using mass fractions, the equation needs to be converted to its mass-based form. The activity coefficient is determined by a combinatorial and residual part, as given in Eqs. 11 and 15, respectively.

By converting the equation to mass-based parameters, one must keep in mind that the surface and volume parameters do not change, nor does the coordination number z. This is because molecules stay the same, no matter what basis is used to determine size, volume or coordination parameters. r_i and q_i are dimensionless parameters for the relative molecular size and surface of component i relative to the size and surface of a CH_2-segment in polyethylene. q_i^* is a dimensionless parameter for the effective surface of molecule i. Since the binary interaction parameters τ_{ij} and τ_{ji} are calculated from interaction energy parameters, these also do not change when converting to mass-based parameters.

Table 1. UNIQUAC Parameters of the Binary Mixture Benzene (1) - 2,2,4-Trimethylpentane (2) as Determined From Sandler[16] and Aspen Plus$^{\mathrm{TM}}$[17]

UNIQUAC Parameter	Benzene	2,2,4-Trimethyl-pentane
z	10	
r_i	3.1878	5.8463
q_i	2.4	5.008
τ_{1i}	1	1.0558
τ_{i2}	0.8054	1

However, it is necessary to redefine the UNIQUAC parameters ϕ_i, θ_i and θ_i^*, so mass-based terms can be used. Since ϕ_i is a volume fraction, the volume term $r_i x_i$ equals the mass term $\frac{w_i}{\rho_i}$, with ρ_i the mass density of the pure component i. This results in the following redefinition of the parameters:

$$\phi_i = \frac{\frac{w_i}{\rho_i}}{\sum_{j=1}^{n}\frac{w_j}{\rho_j}} \qquad (16)$$

$$\theta_i = \frac{\phi_i \frac{q_i}{r_i}}{\sum_{j=1}^{n}\phi_j \frac{q_j}{r_j}} \qquad (17)$$

$$\theta_i^* = \frac{\phi_i \frac{q_i^*}{r_i}}{\sum_{j=1}^{n}\phi_j \frac{q_j^*}{r_j}} \qquad (18)$$

Since $a_i = x_i\gamma_i$, according to Eq. 3, ln a_i can be expressed as

$$\ln a_i = \ln(x_i\gamma_i) = \ln x_i + \ln\gamma_i \qquad (3b)$$

for molar-based parameters, or, when using mass-based parameters

$$\ln a_i = \ln(w_i\gamma_i') = \ln\ w_i + \ln\gamma_i' \qquad (3c)$$

These equations show there are two ways to calculate the activity, but the numerical value should be the same.

After adding $\ln x_i$ to Eq. 11 and 15, and converting all terms to mass-based parameters, the thermodynamic activity a_i of component i in a multicomponent mixture is given by

$$\ln a_i = \ln\phi_i + \left(\frac{z}{2}\right)q_i \ln\frac{\theta_i}{\phi_i} + l_i - \sum_j \phi_j \frac{r_i}{r_j} l_j + q_i^*\left(1 - \ln\left(\sum_j \theta_j^*\tau_{ji}\right) - \sum_j \frac{\theta_j^*\tau_{ij}}{\sum_k \theta_k^*\tau_{kj}}\right) \qquad (19)$$

with l_i as defined in Eq. 13.

Conversion Validation

To prove the consistency of both molar- and mass-based UNIQUAC equations, literature data have been recalculated. Weissman and Wood[15] experimentally determined the molar activity coefficients for a vapor-liquid equilibrium of benzene and 2,2,4-trimethylpentane at 55°C. To simulate this system with the UNIQUAC equation, information on the UNIQUAC parameters is necessary.

The values for the volume and surface parameters r and q for these components are retrieved from literature.[16] The coordination number z is chosen as 10, in accordance with literature,[4,12] and the binary interaction parameters τ_{ij} can be determined with the help of Aspen Plus$^{\mathrm{TM}}$ (Aspen Technology, Cambridge, MA[17]). Table 1 gives an overview of the UNIQUAC parameters used.

With these values the ln γ_i are calculated. In Figure 1, the calculated results are compared to the experimental values determined by Weissman and Wood.[15] As can be seen, the results for the calculated and experimental values agree well. Therefore it can be stated that the molar-based UNIQUAC equation is correctly applied.

To validate the mass-based UNIQUAC equation, the experimental data of Weissman and Wood[15] is used to calculate the activities of the mixture components at 55°C with the help of Eq. 3. The feed mole fractions benzene with a known value of the activity are converted to a feed mass fraction benzene with the help of the relation between molar and mass fractions in a mixture, given by

$$w_i = \frac{m_i}{\sum_j m_j} = \frac{n_i M_i}{\sum_j n_j M_j} = \frac{x_i M_i}{\sum_j x_j M_j} = x_i \frac{M_i}{M_t} \qquad (20)$$

where the summations are performed over all components in the mixture (including the membrane), and where m_i is the mass of component i, M_i is the molar mass of component i, and M_t is the average molar mass of the mixture.

For these values of the molar and mass feed benzene concentration, the component activities are determinated with the molar-based UNIQUAC equations (Eqs. 3, 11, and 15) and the mass-based equations (Eq. 19) respectively. The results of these calculations are given in Tables 2–4.

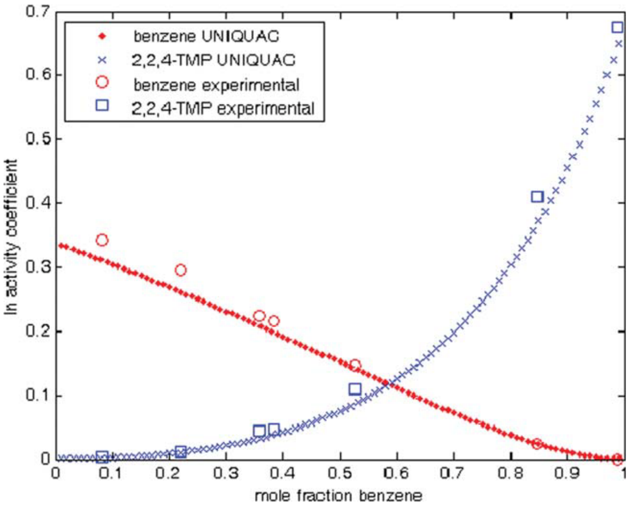

Figure 1. Activity coefficients for the binary mixture benzene–2,2,4-trimethylpentane (2,2,4-TMP) at 55°C.

Experimental data taken from Weissman and Wood.[15] [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 2. Experimental Component Activities for a Mixture of Benzene and 2,2,4-Trimethylpentane (2,2,4-TMP) at Certain Feed Benzene Concentrations

Feed Benzene Mole Fraction	Corresponding Mass Fraction	Experimental Benzene	Activity 2,2,4-TMP
0.0819	0.0575	0.1153	0.9209
0.2192	0.1611	0.2944	0.7894
0.3584	0.2764	0.4480	0.6711
0.3831	0.2981	0.4758	0.6465
0.5256	0.4310	0.6086	0.5294
0.8478	0.7921	0.8673	0.2295
0.9872	0.9814	0.9872	0.0252

Experimental data taken from Weissman and Wood.[15]

To clarify the results, Figure 2 shows the two different calculated component activities together with the values of the component activities determined from the experimental data of Weissman and Wood.[15] From both this figure and Tables 2–4 it can be seen that the calculated and experimental values agree well, proving that the conversion to mass fractions of the UNIQUAC equation is performed correctly. It has to be noted that the mass-based activity coefficients cannot be compared to literature values, since the latter are never described in literature.

Potential Application

As said before, all design methods for fluid mixture separations require quantitative estimates of fluid-phase equilibria. These equilibria can be expressed in terms of activities and activity coefficients, which can be calculated with the help of the UNIQUAC equation. In most membrane processes only liquid–liquid equilibria are involved. An exception however is pervaporation. Fluid-phase equilibria in the pervaporation process are a typical example in membrane process engineering where the UNIQUAC equation based on mass fractions proves useful.

During pervaporation, a liquid (multicomponent) mixture is separated by differential transport through a dense membrane, of which the molar mass usually is unknown or cannot be assigned. Application of a vacuum at the permeate side ensures evaporation of the permeating components over the membrane, due to a partial pressure lower than the saturated vapor pressure of the components. The separation is achieved by different interactions between the selective layer of the membrane and the components. This process was first described by Kober.[18]

Table 3. Molar-Calculated Component Activities for a Mixture of Benzene and 2,2,4-Trimethylpentane (2,2,4-TMP) at Certain Feed Benzene (Molar) Concentrations

Feed Benzene Mole Fraction	Molar-Calculated Benzene	Activity 2,2,4-TMP
0.0819	0.1118	0.9192
0.2192	0.2848	0.7887
0.3584	0.4414	0.6625
0.3831	0.4672	0.6407
0.5256	0.6052	0.5172
0.8478	0.8679	0.2201
0.9872	0.9874	0.0243

Table 4. Mass-Calculated Component Activities for a Mixture of Benzene and 2,2,4-Trimethylpentane (2,2,4-TMP) at Certain Feed Benzene (Mass) Concentrations

Feed Benzene Mass Fraction	Mass-Calculated Benzene	Activity 2,2,4-TMP
0.0575	0.1153	0.9166
0.1611	0.2811	0.7915
0.2764	0.4433	0.6609
0.2981	0.4670	0.6409
0.4310	0.6020	0.5203
0.7921	0.8656	0.2234
0.9814	0.9863	0.0264

Pervaporation can be an alternative for numerous separation applications, but conventionally it is used for separating alcohol-water or organic-organic mixtures. It offers a viable and eco-friendly alternative to some conventional separations, like e.g., destillation.[1,19] Because only the permeating components are evaporated over the membrane, an energy consumption reduction can be achieved. To stimulate industrial application, a prediction of process performance must be made. The UNIQUAC equation can be used to determine sorption into and desorption from the membrane for multicomponent systems.

In pervaporation, the sorption equilibrium at the membrane feed side surface can be considered as a liquid–liquid equilibrium. Although there are not two (partially) immiscible liquids present, inside the membrane the sorbed components behave differently from the feed, since the (dense) membrane is considered to be part of the system[20] and adds to the system interactions. Therefore this equilibrium is described as ''liquid–liquid'' equilibrium.

At the permeate side of the membrane a similar equilibrium exists. However, depending on the position of the phase transition of the permeating components, this is either a ''vapor-liquid'' equilibrium, when the phase transition takes place at the membrane surface, or a ''vapor–vapor'' equilibrium, when the phase transition occurs inside the membrane. In the latter case inside the membrane a vapor-liquid equilibrium needs to be described.

Since the UNIQUAC model is capable of describing all of these different equilibria, it is well-suited to describe phase-equilibria in pervaporation. The UNIQUAC model can be used to calculate equilibrium activities and activity coefficients at the membrane surfaces, and thus to determine the composition inside the membrane. These results can be used for further membrane mass transport description in thermodynamical models.

At the feed side this equilibrium can be considered as a liquid–liquid equilibrium. This means that at the feed side

$$a_i^f \left(= w_i^f \gamma'^f_i\right) = a_i^m \left(= w_i^m \gamma'^m_i\right) \qquad (21)$$

It has to be remarked that inside the membrane (at the surface) an extra component is present, as the membrane is considered to be part of the system. When the composition of the feed and the UNIQUAC parameters are known, the activity of the feed can be calculated. This means the activity inside the membrane is also known and the composition of the permeating components inside the membrane can be itera-

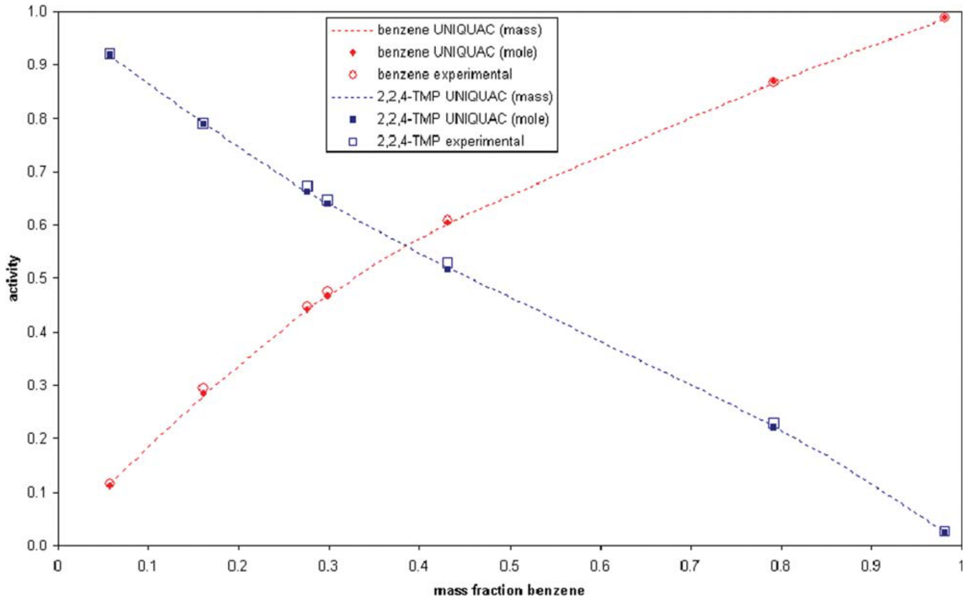

Figure 2. Activities for the binary mixture benzene–2,2,4-trimethylpentane (2,2,4-TMP) at 55°C.

Experimental data taken from Weissman and Wood.[15] [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tively determined (since the activity coefficient is a function of the composition). The fraction of the membrane is then determined by

$$w_m^m = 1 - \sum_{\substack{i \\ i \neq m}} w_i^m \tag{22}$$

The same can be done for the permeate side. However, if the phase transition of the permeating components is assumed to happen at the surface of the membrane, during desorption, this means that at the surface of the membrane a "vapor-liquid" equilibrium is established with the permeate side. In this case the equilibrium is described by

$$a_i^m \left(= w_i^m \gamma_i'^m\right) = a_i^p \tag{23}$$

with a_i^p the activity of the vapor phase. Again, in the membrane one extra component is present in the mixture, and the membrane fraction is determined by Eq. 22.

With this theory, both "liquid–liquid" and "vapor–liquid" sorption isotherms of a ternary mixture of benzene–cyclohexene–cyclohexane in a poly-urethane membrane were constructed, to show the different capabilities of the (converted) UNIQUAC equation. The results are validated with an experimental example of this system at 303.15 K.[12] Since especially for polymer membranes a value for the molar mass of the membrane cannot be assigned, calculations must be performed with mass fractions. Therefore, the mass-based UNIQUAC equation is used. The experimental results are also mass-based.

Because the mixture is ternary, three different binary pairs can be formed. This means that in total six adjustable parameters exist (two per binary pair). To solve the UNIQUAC equation for this system, several parameters are retrieved from literature.[12] Not only the volume and surface parameters for every component are defined, but also the binary interaction parameters between the different component binaries, and between the components and the membrane. The coordination number is still set to 10, and for the membrane the ratio q/r, which can be estimated from structural data, is set to 0.85 in accordance with literature.[12] All UNIQUAC parameters used for the calculations are given in Table 5.

For a ternary system, sorption isotherms of binary mixtures as well as ternary sorption isotherms in the membrane can be determined. Figure 3 shows the liquid sorption isotherms for the binary mixture benzene–cyclohexane in a poly-urethane membrane, compared to literature values. Figure 4 gives the liquid sorption isotherm for the ternary mixture benzene–cyclohexene–cyclohexane in a poly-urethane membrane, when a constant weight fraction of cyclohexene in the feed of 0.1 is assumed. Both figures show good agreement with the experimental values. This means that the sorption algorithm is correctly applied and the mass-based UNIQUAC equation is consistent with experiments.

It can be seen that at higher weight fractions of benzene in the feed, the experimental values for the weight fractions

Table 5. UNIQUAC Parameters of the Ternary Mixture Benzene (1) - Cyclohexene (2) - Cyclohexane (3) in a Poly-urethane Membrane (m) Taken From Enneking et al.[12]

UNIQUAC Parameter		Benzene	Cyclo-Hexene	Cyclo-Hexane
z	10			
$(q/r)_m$	0.85			
r_i		3.188	3.814	4.046
q_i		2.400	3.027	3.240
τ_{1i}		1	1.028	1.073
τ_{2i}		0.888	1	0.818
τ_{3i}		0.777	1.176	1
τ_{im}		0.671	0.483	0.693
τ_{mi}		1.227	1.283	0.883

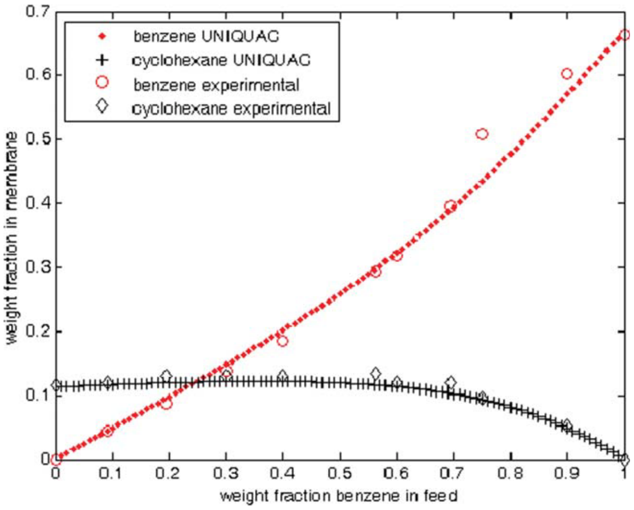

Figure 3. Solubility diagram of the liquid binary mixture benzene–cyclohexane in a poly-urethane membrane at 303.15 K.

Literature data taken from Enneking et al.[12] [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

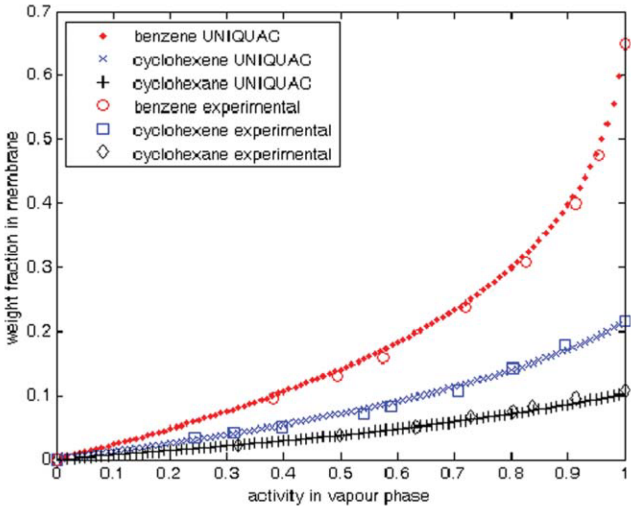

Figure 5. Pure component vapor sorption isotherms for benzene, cyclohexene, and cyclohexane in a poly-urethane membrane at 303.15 K.

Literature data taken from Enneking et al.[12] [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in the membrane for all components exceed the UNIQUAC calculated values. This can have several causes, like membrane swelling, drag and coupling effects, and experimental errors. These phenomena have been researched extensively in membrane technology. It is beyond the scope of this article to explain them here.

These sorption isotherms describe the liquid sorption in a membrane at the feed side of the membrane. At the permeate side desorption can be calculated (which can be seen as "inverted" sorption). If the membrane process is pervaporation and the phase transition occurs within the membrane, the result would be vapor sorption isotherms.

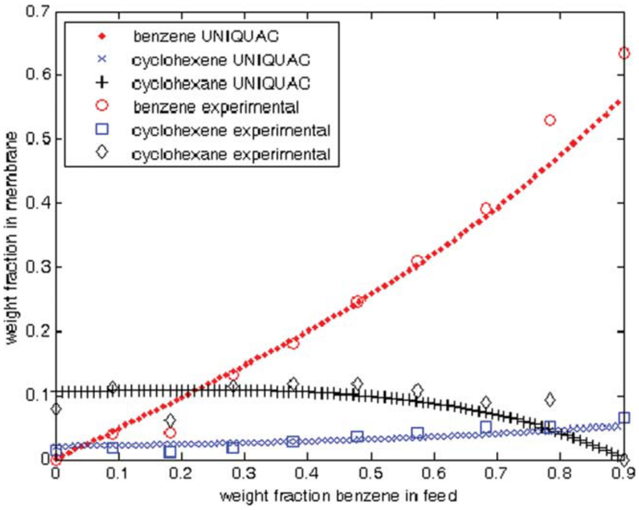

Figure 4. Solubility diagram of the liquid ternary mixture benzene–cyclohexene–cyclohexane in a poly-urethane membrane at 303.15 K and a constant feed cyclohexene fraction of 0.1.

Literature data taken from Enneking et al.[12] [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As described earlier, for a given activity in the vapor at the permeate side, the composition inside the membrane can be calculated. Figure 5 shows three pure-component vapor sorption isotherms for benzene, cyclohexene and cyclohexane in a poly-urethane membrane at 303.15 K. The experimental values are also given. This figure shows again that there is a good agreement between calculated and experimental values, proving consistency of the mass-based UNIQUAC equation with experiments. Thus, the equation derived above allows describing both the sorption and desorption step in pervaporation correctly.

Of course the UNIQUAC equation can be used to determine more phase equilibria and properties. However, the above described examples already state the correctness of the conversion and show the potential of the UNIQUAC equation in membrane process simulation. Therefore, no further examples are given here.

Conclusions

Conversion of the UNIQUAC equation to a mass-based equation is very useful in membrane process engineering. Because mass-based activity coefficients are calculated, weight fractions can be used to overcome the problem of an unknown membrane molar mass.

This research describes this conversion, and also proves consistency between the molar- and mass-based equations. Several tests show good agreement between the molar- and mass-based models, as with literature data. They also show the potential of the UNIQUAC model in membrane process modelling by means of different applications.

Notation

a = thermodynamic activity (-)
g^E = excess Gibbs energy per mole of mixture (J mol^{-1})
l = UNIQUAC parameter (-)
M = molar mass (kg mol^{-1})
M_t = total mixture molar mass (kg mol^{-1})
m = mass (kg)
n = number of moles (mol)
n_t = total number of moles (mol)
q = UNIQUAC surface parameter (-)
q^* = UNIQUAC surface parameter (-)
r = UNIQUAC volume parameter (-)
R = universal gas constant (= 8.3145 J mol^{-1} K^{-1})
T = temperature (K)
u_{ij} = UNIQUAC (interaction) energy parameter (J mol^{-1})
w = weight fraction (-)
x = mole fraction (-)
z = UNIQUAC coordination number (-)

Greek letters

γ = molar-based activity coefficient (-)
γ' = mass-based activity coefficient (-)
θ = UNIQUAC surface fraction (-)
θ^* = UNIQUAC surface fraction (-)
ρ = mass density (kg m^{-3})
τ_{ij} = UNIQUAC binary interaction parameter (-)
ϕ = UNIQUAC volume fraction (-)

Subscripts

i = component i
j = component j
k = component k
m = membrane
n = constant number of moles
P = constant pressure
t = total mixture
T = constant temperature

Superscripts

f = at the feed side
m = inside the membrane
p = at the permeate side

Operators

$\frac{\partial}{\partial}$ = partial derivative
$\sum_{i}$ = sum over all particles i
$\sum_{\substack{i\\ i\neq j}}$ = sum over all particles i with exception of $i = j$

Literature Cited

1. Van Hoof V, Van den Abeele L, Buekenhoudt A, Dotremont C, Leysen R. Economic comparison between azeotropic distillation and different hybrid systems combining distillation with pervaporation for the dehydration of isopropanol. *Sep Purifi Technol*. 2004;37:33–49.
2. Huang HJ, Ramaswamy S, Tschirner UW, Ramarao BV. A review of separation technologies in current and future biorefineries. *Sep Purifi Technol*. 2008;62:1–21.
3. Ravanchi MT, Kaghazchi T, Kargari A. Application of membrane separation processes in petrochemical industry: a review. *Desalination*. 2009;235:199–244.
4. Abrams DS, Prausnitz JM. Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J*. 1975;21:116–128.
5. Hoch G, Chauhan A, Radke CJ. Permeability and diffusivity for water transport through hydrogel membranes. *J Memb Sci*. 2003; 214:199–209.
6. Wesselingh JA, Bollen AM. Multicomponent diffusivities from the free volume theory. *Chem Eng Res Des*. 1997;75:590–602.
7. Hogendoorn JA, van der Veen AJ, van der Stegen JHG, Kuipers JAM, Versteeg GF. Application of the Maxwell-Stefan theory to the membrane electrolysis process: Model development and simulations. *Comput Chem Eng*. 2001;25:1251–1265.
8. Cunha VS, Paredes MLL, Borges CP, Habert AC, Nobrega R. Removal of aromatics from multicomponent organic mixtures by pervaporation using polyurethane membranes: experimental and modeling. *J Memb Sci*. 2002;206:277–290.
9. Heintz A, Stephan W. A generalized solution-diffusion model of the pervaporation process through composite membranes Part I. Prediction of mixture solubilities in the dense active layer using the UNIQUAC model. *J Memb Sci*. 1994;89:143–151.
10. Izák P, Bartovská L, Friess K, Šípek M, Uchytil P. Comparison of various models for transport of binary mixtures through dense polymer membrane. *Polymer*. 2003;44:2679–2687.
11. Izák P, Bartovská L, Friess K, Šípek M, Uchytil P. Description of binary liquid mixtures transport through non-porous membrane by modified Maxwell-Stefan equations. *J Memb Sci*. 2003;214: 293–309.
12. Enneking L, Heintz A, Lichtenthaler RN. Sorption equilibria of the ternary mixture benzene/cyclohexene/cyclohexane in polyurethane- and PEBA-membrane polymers. *J Memb Sci*. 1996;115:161–170.
13. Bausa J, Marquardt W. Detailed modeling of stationary and transient mass transfer across pervaporation membranes. *AIChE J*. 2001;47:1318–1332.
14. Prausnitz JM, Lichtenthaler RN, de Azevedo EG. *Molecular Thermo-Dynamics of Fluid-Phase Equilibria*, 2nd ed. Englewood Cliffs NJ: Prentice Hall, 1986.
15. Weissman S, Wood SE. Vapor-liquid equilibrium of benzene-2,2,4-trimethylpentane mixtures. *J Chem Phys*. 1960;32:1153–1160.
16. Sandler S. *Chemical and engineering thermodynamic*, 3rd ed. New York: Wiley; 1999.
17. Aspen Plus$^{\text{TM}}$. *Aspen Engineering Suite*. Aspen Technology Inc., Cambridge, MA; 2007. Available at www.aspentech.com. Accessed in November 2009.
18. Kober PA. Pervaporation, perstillation and percrystallization. *J Am Chem Soc*. 1917;39:944–948.
19. Del Pozo Gomez MT, Klein A, Repke JU, Wozny G. A new energy-integrated pervaporation distillation approach. *Desalination*. 2008;224:28–33.
20. Krishna R, Wesselingh JA. The Maxwell-Stefan approach to mass transfer. *Chem Eng Sci*. 1997;52:861–911.

Manuscript received Oct. 19, 2009, and revision received July 7, 2010.