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Improvement of the UNIQUAC Combinatorial-Entropy Term by Adjusting the Standard Segment

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S Supporting Information

ABSTRACT: A standard segment is used to determine the structural parameters *r* and *q* of the UNIQUAC combinatorial-entropy term. Generally, it is assumed that the choice of the standard segment and the influence of the absolute value of *q* are negligible. The standard segment area, however, does not cancel out in the model equation and, therefore, is a model parameter. In this work this parameter is determined by fitting the model to experimental data of binary *n*-alkane mixtures. To account for residual effects of the *n*-alkane mixtures, a suitable correlation was developed. From the fit a new standard segment resulted, which is about a factor of 3 smaller than the original UNIQUAC standard segment. The new standard segment significantly improves the performance of the UNIQUAC combinatorial-entropy term.

INTRODUCTION

G^E models describe the activity of the components in a liquid mixture. These models can, therefore, be used to describe the vapor−liquid or liquid−liquid equilibrium. The knowledge of these phase equilibria is often of great significance for process synthesis or process simulation. UNIQUAC (UNIversal QUASIchemical) is an established G^E model often used by process engineers. It was first published by Abrams and Prausnitz in 1975. In 1978 Maurer and Prausnitz presented the model again after revising the derivation of the model equation.[1]

In UNIQUAC the Gibbs energy is separated into a combinatorial and a residual term:

$$G^E = G^E_{\text{comb}} + G^E_{\text{res}} \tag{1}$$

The residual term accounts for energetic effects in the mixture while the combinatorial term considers steric effects in the mixture that depend on molecular volume and surface area to a first approximation. In UNIQUAC the combinatorial contribution is described with the Staverman−Guggenheim equation. To investigate the effect of the combinatorial term, UNIQUAC can be tested for components where only minor contributions to G^E due to interaction forces are to be expected, e.g., *n*-alkanes. Such a comparison was performed by Kikic et al.[2] It was found that the original Staverman−Guggenheim equation has difficulties describing, e.g., the infinite-dilution activity coefficients in alkane mixtures. Thus an exponent was introduced in the definition of the surface fraction of a component to overcome this difficulty. Such an exponent had first been proposed by Donohue and Prausnitz[3] and was also considered in the various versions of UNIFAC in use today.[2,3] Since such a more or less empirical modification is not satisfactory, in this work we investigate the historical development of the combinatorial term as applied in today's models and try to derive a physically well-founded alternative.

COMBINATORIAL TERM

Staverman and Guggenheim both derived an expression for the combinatorial entropy of a mixture.[4,5] For the excess entropy both models lead to the same expression

$$S^E_{\text{comb}} = -R\sum_i^{N_c} x_i \ln\frac{\phi_i}{x_i} - \frac{1}{2}R\sum_i^{N_c} zq_ix_i \ln\frac{\psi_i}{\phi_i} \tag{2}$$

where N_c is the number of components in the mixture, R the universal gas constant, z is the coordination number resulting from the lattice picture of the liquid applied and x_i the mole fraction of component i. The volume fraction ϕ_i and the surface-area fraction ψ_i are defined in terms of the structural parameters r and q as

$$\phi_i = \frac{x_ir_i}{\sum_j^{N_c} x_jr_j} \tag{3}$$

and

$$\psi_i = \frac{x_iq_i}{\sum_j^{N_c} x_jq_j} \tag{4}$$

where r and q describe the van der Waals volume and area of the molecule relative to those of a standard segment

$$r_i = \frac{V_{\text{vdW},i}}{V_{\text{vdW,ref}}} \tag{5}$$

$$q_i = \frac{A_{\text{vdW},i}}{A_{\text{vdW,ref}}} \tag{6}$$

For $V_{\text{vdW},i}$ and $A_{\text{vdW},i}$ Abrams and Prausnitz[6] proposed to use the values determined with the group-increment method of

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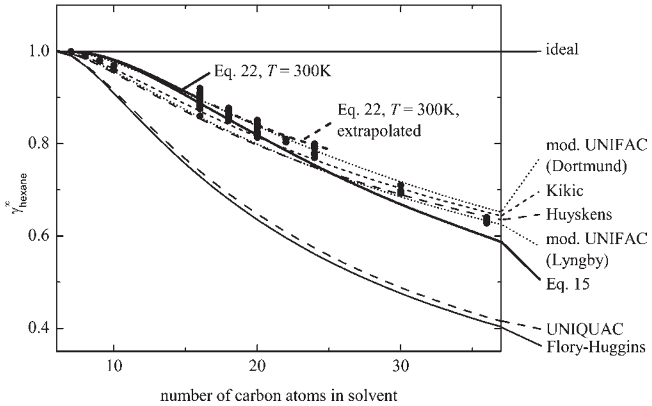

Figure 1. Comparison of the different combinatorial terms and eq 22 with experimental data of the activity coefficient of *n*-hexane at infinite dilution in other *n*-alkanes. All experimental data were taken from the DECHEMA data series.[8]

Bondi.[7] The standard segment is regarded as a sphere with radius r_{ref}, so its volume is given by

$$V_{\text{vdW, ref}} = \frac{4}{3} N_A \pi r_{\text{ref}}{}^3 \tag{7}$$

and surface area by

$$A_{\text{vdW, ref}} = 4 N_A \pi r_{\text{ref}}{}^2 \tag{8}$$

N_A is the Avogadro constant. Abrams and Prausnitz have chosen the standard segment for the UNIQUAC combinatorial term such that it satisfies the identity

$$\frac{z}{2}(r - q) = r - 1 \tag{9}$$

for a linear polymethylene molecule of infinite length. This choice is arbitrary and leads to[6]

$$r_{\text{ref}} = 1.818 \times 10^{-10} \text{ m} \tag{10}$$

To be able to directly compare the performance of different models to reality in Figure 1, a comparison with activity coefficients at infinite dilution is shown. Kikic et al.[2] investigated the UNIQUAC combinatorial term and found that the degree of nonideality predicted by the model is greatly exaggerated for some binary alkane mixtures. This can also be seen in Figure 1. Therefore, they proposed a modification of the UNIQUAC combinatorial term analogous to a modification proposed by Donohue and Prausnitz[3] of the Flory and Huggins term:

$$S^{\text{E}}_{\text{comb}} = -R \sum_i^{N_c} x_i \ln \frac{\phi_i^{\text{Kikic}}}{x_i} - \frac{1}{2} R \sum_i^{N_c} z q_i x_i \ln \frac{\psi_i}{\phi_i} \tag{11}$$

$$\phi_i^{\text{Kikic}} = \frac{x_i r_i{}^{2/3}}{\sum_j^{N_c} x_j r_j{}^{2/3}} \tag{12}$$

The exponent 2/3 was determined by comparison with experimental data. This modification greatly improves the performance of the model, which only slightly overestimates the nonidealities of shorter *n*-alkanes, as can be seen in the figure.

Huyskens and Haulait-Pirson[9] state that many authors are aware that the Flory–Huggins term does not describe reality quite correctly, as also seen in Figure 1. The Flory–Huggins term like the UNIQUAC combinatorial term strongly overestimates the nonidealities of the mixture. They realized that reality lies somewhere between the ideal solution and the Flory–Huggins equation and thus write

$$S^{\text{E}}_{\text{comb}} = -R \frac{1}{2} \sum_i^{N_c} x_i \ln \frac{\phi_i}{x_i} \tag{13}$$

They show that this equation yields better results for solubilities of solid *n*-alkanes in liquid alkanes than the ideal solution term or the Flory–Huggins term alone. Their equation is simple and yields clearly improved results, as shown in Figure 1 although most nonidealities are overestimated.

Weidlich and Gmehling proposed a modification similar to that of Kikic et al., but instead of an exponent of 2/3 they used 3/4 for their modified UNIFAC (Dortmund) model.[10] This value resulted from a fit of the activity coefficient at infinite dilution to experimental data of mixtures of alkane + alkane, alkane + alcohol, and alcohol + alcohol. The parameters *r* and *q* they use are determined from different group contributions. These group contributions for the parameters *r* and *q* were also obtained from a fit to experimental data and are no longer calculated from molecular parameters as in UNIQUAC. Thus pure-component parameters have in effect been fitted to mixture data, which may be causing inconsistencies in principle. Figure 1 shows that the model reproduces the experimental data very well. It should be noted, however, that for the modified UNIFAC (Dortmund) model the introduced modifications to the structure of the model are merely empirical.

Larsen et al proposed to use for their modified UNIFAC (Lyngby) model an altered Flory–Huggins combinatorial term with modified volume fractions following Kikic et al.:[11]

$$S^{\text{E}}_{\text{comb}} = -R \sum_i^{N_c} x_i \ln \frac{\phi_i^{\text{Kikic}}}{x_i} \tag{14}$$

instead of using the Staverman–Guggenheim combinatorial term. The volume parameters *r* are calculated as in UNIQUAC.[11] They argue that the Staverman–Guggenheim term represents a corrected Flory–Huggins term, which they correct in an alternative way as specified in eq 14. The correcting contribution of the last term of eq 2 is said to be often quite small, but it may, however, in some cases give large corrections, even leading to negative values of the combinatorial excess entropy, which are not considered realistic. Figure 1 shows that the modified UNIFAC (Lyngby) model performs similarly to the Huyskens model, overestimating almost all nonidealities.

MODIFICATION OF THE UNIQUAC COMBINATORIAL TERM

Pfennig[12] investigated the Guggenheim combinatorial entropy term by comparing results from this model with results from lattice based computer simulations. It was shown that the model performs perfectly well for unflexible chain molecules. This was not surprising, since the Guggenheim model was derived exactly for such a lattice system and molecules that do not fold back on themselves. This agreement between lattice simulation and the Guggenheim model shows though that the model equation is in principle well suited to describe the combinatorial contribution of chain molecules in a mixture. Thus one would not necessarily expect that changing the model structure in an empirical fashion would improve performance.

The question thus arises why good results are obtained when the Staverman–Guggenheim model is compared to results from computer simulations and why the UNIQUAC combinatorial

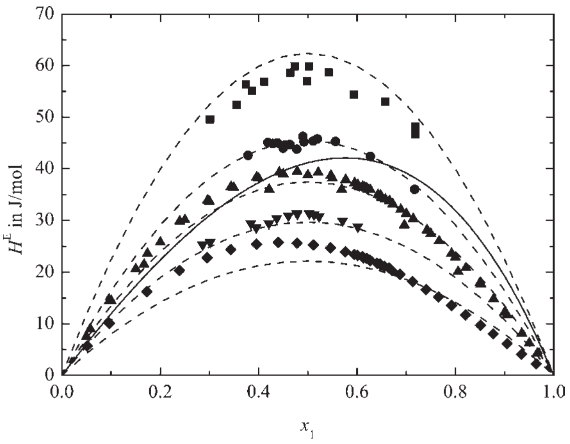

Figure 2. Comparison of experimental heat of mixing data with results from eq 18 (dashed lines) and eq 16 (solid line) for the binary *n*-hexane (1) + *n*-dodecane (2) mixture: ■, 283.15 K; ●, 293.15 K; ▲, 298.15 K; ▼, 303.15 K; ◆, 308.15 K. All experimental data taken from DECHEMA data series.[13]

term compares badly with experimental results? Having a closer look at eqs 3 and 4 reveals that the reference volume and area cancel out in those equations, while it does not in eq 6. Therefore, the second term in eq 2 depends upon the choice of the standard segment. z is usually set to 10, which is not problematic, since it is zq_i that needs to be determined meaningfully. As a consequence of these considerations $A_{\text{vdW,ref}}$ should actually be regarded as a model parameter that cannot be set arbitrarily. Thus instead of using $A_{\text{vdW,ref}}$ as chosen arbitrarily by Abrams and Prausnitz, it should be replaced by a general reference surface area A^* as a new standard segment.

To keep the change to the model equation minimal, eq 2 can be written as

$$S^{\text{E}}_{\text{comb}} = -R\sum_{i}^{N_c} x_i \ln\frac{\phi_i}{x_i} - \frac{1}{2}R\sum_{i}^{N_c} z\frac{A_{\text{vdW, ref}}}{A^*} q_i x_i \ln\frac{\psi_i}{\phi_i} \qquad (15)$$

where furthermore q_i, ϕ_i, and ψ_i are determined as in UNIQUAC.

The new reference surface then needs to be determined by fitting eq 15 to experimental data of molecules, which differ in size. It is then assumed that this value does not depend any further on the system investigated and can be regarded as a general constant in the equation. For fitting A^* it has to be observed that the combinatorial term does not take any energetic effects of mixtures and pure components into account. Therefore, data of mixtures that behave nearly athermally should be used for the fit, since then the influence of A^* should be maximum.

■ EXPERIMENTAL DATA

No real binary mixture behaves absolutely athermally. Mixtures of *n*-alkanes, however, behave nearly athermally while the molecules differ in size, leading to a contribution to combinatorial entropy. These mixtures were thus used to determine the reference surface of the new standard segment. Figure 2 shows, e.g., the heat of mixing of a binary mixture consisting of *n*-hexane and *n*-dodecane at various temperatures. Note that the heat of mixing is small but that a significant temperature dependence is observed. Experimental H^E and γ^∞ data of binary *n*-alkane mixtures were thus used for the fit. All data were taken from the DECHEMA Chemistry Data Series.[8,13]

Table 1. Number of Selected Experimental Data Points of Activity Coefficients at Infinite Dilution of Binary *n*-Alkane Mixtures[a]

	solute						
solvent	C4	C5	C6	C7	C8	C9	C10
C5	0	0	0	0	1	0	0
C6	0	1	0	0	0	0	0
C7	0	2	6	0	1	0	0
C8	0	6	3	0	0	0	0
C9	0	1	1	0	0	0	0
C10	0	0	5	0	0	0	0
C12	0	8	0	0	0	0	0
C16	4	14	60	35	13	9	2

[a] Temperature range between 280.15 K and 453.15 K.

As chain length increases for *n*-alkanes, the molecular flexibility can lead to a back bending of the chain to form intramolecular contacts. This changes the number of external contacts zq_i of a molecule, as discussed in Pfennig.[12] The flexibility of molecules is not accounted for in the Staverman−Guggenheim combinatorial term as it is used here, so to obtain accurate results, data of long *n*-alkanes have to be omitted from the fit. Analyzing the tendency for backbending simulated with a geometric molecular model showed that the effect on zq_i may still be acceptable for *n*-hexadecane[12] and since many data for systems with *n*-hexadecane are available, *n*-hexadecane was still included in the fit. Thus *n*-butane was the shortest and *n*-hexadecane the longest *n*-alkane considered.

All data used for the fit were carefully selected. The selection procedure of the γ^∞ data consisted of performing a preliminary fit of eq 15 to all the data for one solute and comparing the model results with the experimental values. First it was checked whether the model shows systematic deviations, e.g., that the model underestimates the experimental values for short solvents and overestimates them for long solvents. Such behavior was not detected, so in a next step the data points for individual solvents were considered. When a data point clearly differed from the others, it was excluded from the data set. If several data points from the same reference were found to deviate from the rest, all of the data points of that reference were excluded from the fit, since in this case systematical errors in the remaining data points cannot be excluded.

Since a considerable amount of data is needed to determine whether the model shows systematic deviations or a data point differs from the rest, this selection procedure could only be performed for the solutes *n*-pentane up to *n*-octane. For the other solutes the model was fitted to the data for *n*-pentane to *n*-octane and then extrapolated. Since the model is extrapolated, the selection criteria for those solutes were relaxed slightly. In total about 23% of the original data were excluded by the selection procedure.

The H^E data cannot be easily assessed graphically since, in addition to the temperature and the type of components, the composition of the mixture varies. Instead of evaluating all data of mixtures with one common component simultaneously, all binary systems were evaluated individually. To do so, all data points of a binary system were plotted in a single diagram. If enough data points were available to unambiguously identify data points that differ from the rest, these data points were excluded from the data set.

Table 1 shows the number of data points of activity coefficients at infinite dilution that were used for the fit after the

Table 2. Number of Selected Experimental Data Points of Heat of Mixing of Binary *n*-Alkane Mixtures[a]

	component 2				
component 1	C7	C8	C10	C12	C16
C5	0	0	3	0	0
C6	22	13	88	42	172
C7	0	0	0	19	16
C8	0	0	0	30	3
C10	0	0	0	19	4

[a] Temperature range between 283.15 K and 349.15 K.

selection procedure. The temperature varies between 280.15 K and 453.15 K. Table 2 shows the number of selected experimental data points of the heat of mixing of binary *n*-alkane mixtures. The temperature range varies between 283.15 K and 349.15 K.

RESIDUAL TERM

Although the heat of mixing of *n*-alkane mixtures is small, it still has to be accounted for when the reference surface of the new standard segment is to be determined accurately. Also certain entropic excess contributions have to be considered, as discussed by Patterson et al.[14,15] Therefore, the new combinatoric term of eq 15 is supplemented with a residual term intended to cover these effects. The residual term is developed empirically and only to reproduce well the selected experimental data for this work. The resulting model is then fitted to the selected experimental data to obtain the value for the reference surface of the new standard segment.

The residual term was developed on the basis of a simple regular solution model, in which CH_2 and CH_3 segments of *n*-alkanes are differentiated energetically. For a binary mixture this model reads

$$H^{E} = \frac{1}{2}\, z\tilde{\omega} q_1 q_2 \frac{x_1 x_2}{x_1 q_1 + x_2 q_2}(\theta_{13} - \theta_{23})^2 \tag{16}$$

θ_{i3} is the surface fraction of the CH_3 groups in the molecule *i*. $z\tilde{\omega}$ characterizes the interchange energy. $\tilde{\omega}$ is defined by

$$\tilde{\omega} = 2\varepsilon_{23} - \varepsilon_{22} - \varepsilon_{33} \tag{17}$$

where ε_{23} represents the interaction energy between a CH_2 and a CH_3 group. ε_{22} and ε_{33} represent the interaction energy between two CH_2 and two CH_3 groups respectively.

It was shown by de Matos Alves[16] that eq 16 shows systematic errors when describing the heat of mixing of the selected *n*-alkane mixtures. These systematic errors result from the fact that eq 16 produces asymmetric curves when plotted over x_1 whereas most of the excess enthalpy data is symmetric. For example, Figure 2 shows the heat of mixing of the system *n*-hexane + *n*-dodecane. In the figure it can be seen that the deviation from a symmetric course is small.

Analysis showed that the overestimated asymmetry is the result of the denominator in eq 16. Thus to avoid overestimated asymmetry of the model, the denominator of eq 16 was omitted, which can be regarded as skipping the q_i in the denominator. With the available experimental H^E data a correlation for $\tilde{\omega}$ was then developed as a function of *T* and q_i. To do so, several plots of the experimental data over different variables were studied and from the plots several correlations were derived which were all further investigated. The best results were obtained with the following equation:

$$H^{E}_{\text{res}} = \frac{1}{2}\, z x_1 x_2 q_1 q_2 (\theta_{13} - \theta_{23})^2 \left(a + b(q_1 - q_2){q_1}^2 + \frac{c}{T} \right) \tag{18}$$

where *a*, *b*, and *c* are parameters. Equation 18 was integrated according to the Gibbs−Helmholtz equation

$$\left(\frac{\partial \left(\frac{G^{E}}{T} \right)}{\partial T} \right)_{p,x_i} = -\frac{H^{E}}{T^2} \tag{19}$$

to obtain the residual Gibbs energy term. The integration constant was derived using the fact that for

$$\hat{T} = -\frac{c}{a + b(q_1 - q_2){q_1}^2} \tag{20}$$

$H^{E}_{\text{res}}(x_1,\hat{T})$ equals zero for all x_1. This means that at $T = \hat{T}$ the mixture behaves ideally, since it shows no heat of mixing. Because of the lack of energetic effects in the mixture at this temperature, no energy related entropy effects can occur. This leads to the condition that $S^{E}_{\text{res}}(x_1,T)$ and, therefore, $G^{E}_{\text{res}}(x_1,T)$ must equal zero at $T = \hat{T}$. With this condition the integration constant was determined. $G^{E}_{\text{res}}(x_1,T)$ resulted in

$$G^{E}_{\text{res}} = \frac{1}{2}\, z x_1 q_1 x_2 q_2 (\theta_{13} - \theta_{23})^2 \left(a + b(q_1 - q_2){q_1}^2 + \frac{c}{T} - T\left(\frac{c}{2T^2} - \frac{\left(a + b(q_1 - q_2){q_1}^2\right)^2}{2c} \right) \right) \tag{21}$$

Fitting the parameters *a*, *b*, and *c* to the selected experimental H^E data results in an average absolute deviation of 3.51 J/mol per data point. Figure 2 shows a comparison of experimental heat of mixing data with results from eq 18 for the binary *n*-hexane + *n*-dodecane system. The correlation describes the experimental data well. Especially the temperature dependence is properly depicted. Only at the lowest temperature are the experimental data slightly overestimated, and at the highest temperature the correlation shows a slight deviation due to the asymmetry of the experimental data, which cannot be represented by the model.

Comparing the result with eq 16, which is also included in Figure 2 shows that eq 18 is a considerable improvement, since eq 16 cannot describe asymmetry nor temperature dependence properly. At the same time it should be stressed here that we only seek a suitable expression taking the excess over the combinatorial contribution into account as good as possible to gain deeper insight into the behavior of the combinatorial models available. Thus we regard eq 18 as some auxiliary function with little molecular thermodynamic meaning, but with the ability to represent the data well with a minimal number of parameters.

RESULTS AND DISCUSSION

Combining the modified combinatorial model eq 15 with the residual term of eq 21 according to eq 1 results in

Table 3. Mean Squared Residual for the Different Combinatorial Terms and for the Model Used in This Work

model	γ^∞, %	H^E, J/mol
UNIQUAC[6]	15.22	
Huyskens[9]	5.12	
Kikic[2]	3.88	
modified UNIFAC (Dortmund)[10]	2.52	
modified UNIFAC (Lyngby)[11]	4.87	
this work, eq 22	2.26	3.59
this work, only the combinatorial part of eq 22	2.15	

$$G^E = \frac{1}{2} z x_1 q_1 x_2 q_2 (\theta_{13} - \theta_{23})^2$$

$$\left(a + b(q_1 - q_2){q_1}^2 + \frac{c}{T} - T\left(\frac{c}{2T^2} - \frac{(a + b(q_1 - q_2){q_1}^2)^2}{2c}\right)\right)$$

$$+ RT \sum_i^{N_c} x_i \ln \frac{\phi_i}{x_i} + \frac{1}{2} RT \sum_i^{N_c} z \frac{A_{\text{vdW, ref}}}{A^*} q_i x_i \ln \frac{\psi_i}{\phi_i} \tag{22}$$

The reference surface of the new standard segment A^* and the correlation parameters a, b, and c were then fitted to the selected H^E and γ^∞ data simultaneously. The Levenberg–Marquardt algorithm (LMDIF)[17] and the objective function

$$\Delta = \frac{1}{\Delta H^E} \sum_i (H^E_{\text{exp}, i} - H^E_{\text{calc}, i})^2 + \frac{1}{\Delta \gamma^\infty} \sum_j \left(\frac{\gamma^\infty_{\text{exp}, j} - \gamma^\infty_{\text{calc}, j}}{\gamma^\infty_{\text{exp}, j}}\right)^2 \tag{23}$$

where used.

The H^E data were fitted on the basis of absolute deviations, because when relative deviations are used, the fit tends to reproduce systems with small H^E values much better than systems with higher H^E values. The γ^∞ data were fitted on the basis of relative deviations. The contributions of H^E to the objective function were weighted with a factor

$$\Delta H^E = \sum_i (H^E_{\text{exp}, i} - H^E_{\text{calc}, i})^2 \tag{24}$$

which equals the sum of squared residuals resulting from fitting eq 22 only to the experimental H^E data. The contributions of γ^∞ to the objective function were weighted with

$$\Delta \gamma^\infty = \sum_j \left(\frac{\gamma^\infty_{\text{exp}, j} - \gamma^\infty_{\text{calc}, j}}{\gamma^\infty_{\text{exp}, j}}\right)^2 \tag{25}$$

which equals the sum of squared residuals resulting from fitting eq 22 only to the experimental γ^∞ data. In this way the different number of data for the different properties as well as their considerably different magnitude of deviation are accounted for.

Table 3 shows the mean squared residuals for the different combinatorial terms. Also Table 3 shows the mean squared residuals for eq 22 after the fit as well as the mean squared residual of only the combinatorial part of eq 22 after the fit.

The new model describes the selected γ^∞ and H^E data very well. The fit is better than any other model for the combinatorial contribution. Evaluating only the combinatorial part of eq 22 shows a slightly smaller mean squared residual for the γ^∞ data compared to the complete model. This small difference confirms that the none-combinatorial contribution to γ^∞ for n-alkane mixtures is small, which is why these mixtures were chosen for the fit. Because of the good description of H^E including its temperature dependence, also the small residual part of the γ^∞ data is well described. As a consequence it can be assumed that the new reference segment for the combinatorial contribution is determined significantly from the data.

Table 4. Resulting Values for the Parameters of eq 22

parameter	value
a	-3.031×10^2 J/mol
b	-3.413×10^{-1} J/mol
c	9.355×10^4 J K/mol
A^*	1.932×10^4 m^2/mol

Equation 22 as well as the combinatorial part of eq 22, eq 15, have been included in Figure 1. From the comparison of the full model with only the combinatorial part of eq 22 it can be seen that the contribution by the residual part of eq 22 is small. Since the residual part of eq 22 is temperature dependent, the model was only plotted for 300 K, whereas the experimental data vary between 293.15 K and 453.15 K. Equation 22 was fitted to experimental data of n-alkanes with up to 16 carbon atoms. The full eq 22 has, therefore, only been extrapolated for up to 25 carbon atoms in the solvent, since it cannot be expected that the empirically formulated residual part of eq 22 can be extensively extrapolated.

The other models only consider the combinatorial contribution. To allow a fair comparison, the combinatorial part of eq 22 was plotted over the whole range with the reference surface as determined from the fit of eq 22. It is obvious that the combinatorial part of eq 22 describes the data well, although it was not fitted directly to the data and only data from mixtures with n-alkanes with up to 16 carbon atoms were considered for the fit. It should be especially stressed that the characteristic general slope as a function of carbon number is better described as compared to the other models. While compared to the other models the experimental data typically lie above the models for low carbon numbers and tend to lie below the models for higher carbon number—at least if the data for low carbon number are better described—the overall behavior is better depicted by the combinatorial part of eq 22 with the new reference segment.

The difference between the combinatorial part of eq 22 and the Flory–Huggins model is due to the second term of eq 15. This term of the Staverman–Guggenheim equation is often considered a higher order correction term usually assumed to be small. However, it is shown here that this term is not negligible if applied properly. The result shows that a meaningfully determined reference segment for the UNIQUAC combinatorial term, while maintaining the physically founded form of the equation, leads to an at least as good result compared to the purely empirical modifications of the original models.

Table 4 shows the parameters of eq 22, which resulted from the fit. The new reference surface is 0.1932×10^9 cm^2/mol corresponding to a radius of 5.053×10^{-2} nm. These values are significantly less than those of the reference segment originally obtained for UNIQUAC, which was characterized by a radius of 1.818×10^{-1} nm and a surface area of 2.5×10^9 cm^2/mol. According to Bondi, the van der Waals radius of a hydrogen atom equals 1.20×10^{-1} nm.[18] The new standard segment is a little less than half the size of a hydrogen atom. We believe that this size can be regarded as the order of the geometrical dimension at which molecules "feel" their geometric details. Considering the fact that on the surface of a molecule at the intersection between two covalent bonded atoms smaller radii than the van der Waals radii of the atoms can occur, this appears to be reasonable.

Also the standard segment not only determines the segmentation of the molecules but also determines the segmentation of space. The new, smaller standard segment leads to a higher number of possible arrangements of the molecules of a system. This must be considered closer to reality than the result with the original standard segment, since in reality there is in principle an infinite number of possible arrangements of the molecules of a system.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** References of the experimental data used for the parameter fit. This material is available free of charge via the Internet at http://pubs.acs.org.

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