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Application of Simplified PC-SAFT to Glycol Ethers

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ABSTRACT: The simplified PC-SAFT (sPC-SAFT) equation of state is applied for binary glycol ether-containing mixtures, and it is investigated how the results are influenced by inclusion of intramolecular association in the association theory. Three different glycol ethers are examined: 2-methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol. Vapor—liquid and liquid—liquid equilibria of miscible and immiscible, self- and cross-associating mixtures are considered, including the closed-loop liquid—liquid equilibrium of 2-butoxyethanol—water. The results are finally compared to other association models.

INTRODUCTION

Glycol ethers are nonionic surfactants with a variety of industrial applications, including a number of applications in the petroleum industry. Glycol ethers contain one hydroxyl group and one or more ether oxygens, and they are the simplest real compounds that can form intramolecular hydrogen bonds. Glycol ethers are therefore interesting candidates for testing the new theory for intramolecular association for SAFT type equations of state[1−3] (EoS) presented in the Ph.D. thesis by Avlund[4] and in a recently published paper.[5]

A lattice theory, which accounts for both inter- and intramolecular association for polyethoxyalcohols, was presented in 1999 by Missopolinou and Panayiotou,[6] and the theory has been applied for glycol ethers in a number of papers.[7−9]

Because a general theory for intramolecular association in the framework of SAFT was only recently developed, all work with SAFT type EoS so far has been done without considering intramolecular association (explicitly). Garrido et al.[10] have applied CPA for different binary mixtures of glycol ethers, both self- and cross-associating mixtures, and Garcia-Lisbona et al.[11] have applied SAFT-HS for 2-butoxyethanol—water.

We have in this work applied sPC-SAFT[12] for binary glycol ether-containing mixtures. Calculations have been done both with and without inclusion of the new theory for intramolecular association. We have considered miscible and immiscible, self- and cross-associating mixtures.

INTRAMOLECULAR ASSOCIATION

The association theory used in SAFT only accounts for intermolecular association, but for some systems it is important also to consider the intramolecular interactions. While intermolecular association is interaction between different molecules that are bonded to form dimers or larger chain- or tree-like clusters, intramolecular association is interaction between sites on the same molecule, which leads to the formation of ring structures. The difference between inter- and intramolecular association is illustrated in Figure 1.

Spectroscopy data presented by Brinkley and Gupta[13] and Missopolinou et al.[7] have, for dilute mixtures of glycol ethers in n-hexane, shown that intramolecular association is dominating as compared to intermolecular association at low glycol ether concentrations. Figure 2 shows the amount of inter- and

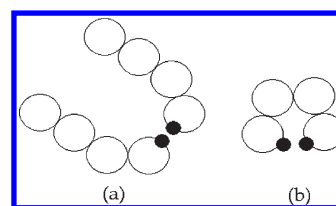**Figure 1.** (a) Intermolecular and (b) intramolecular association of model chain molecules.
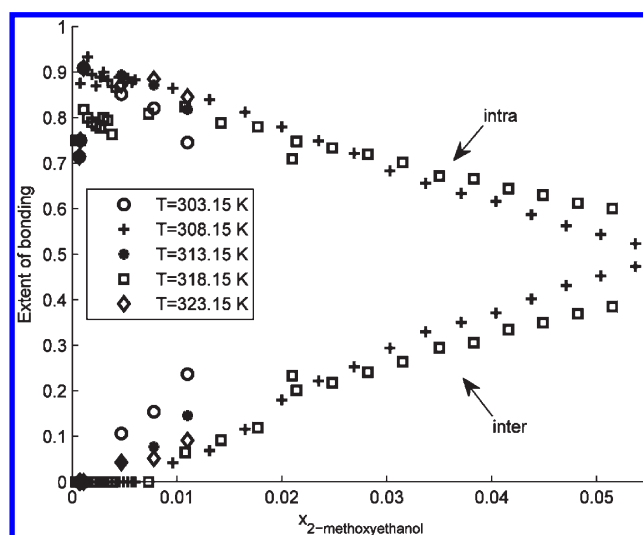

Figure 2. Amount of hydrogen bonds for 2-methoxyethanol—n-hexane, from FT-IR spectroscopy. Experimental data: Brinkley and Gupta[13] (T = 308.15 and 318.15 K) and Missopolinou et al.[7] (T = 303.15, 313.15, and 323.15 K).

intramolecular hydrogen bonds for 2-methoxyethanol—n-hexane, measured with FT-IR spectroscopy.

The spectroscopy data show that as the concentration of the glycol ether decreases, the amount of intermolecular bonds also decreases, because the distance between the glycol ether molecules increases, and the probability of being within bonding range of another glycol ether molecule therefore decreases. The intramolecular association does not explicitly depend on concentration (or density), but when the competition from intermolecular association decreases, the amount of intramolecular association increases. It is clear from Figure 2 that there is a large amount of intramolecular bonds in the dilute solution of 2-methoxyethanol in the nonassociating solvent.

A general theory for intramolecular association in the framework of SAFT was presented in a recently published paper by Avlund et al.[5] and in the Ph.D. thesis by Avlund.[4] This theory was developed on the basis of previous work by Sear and Jackson[14] and Ghonasgi and Chapman,[15] who have developed intramolecular association theories for two associating sites.

According to the theory, the contribution to the Helmholtz free energy from association (inter- as well as intramolecular) is for a pure component given by:

$$\tilde{a}^{assoc} = \frac{A^{assoc}}{NkT} = \ln X_0 + \frac{1}{2}\sum_A (1 - X_A) - \frac{1}{2}\sum_A \sum_{B \neq A} X_{AB}\Delta_{AB}^{intra} \tag{1}$$

where X_A is the fraction of molecules not bonded at site A, given by:

$$1 = X_A\left[1 + \rho \sum_B X_B\Delta_{AB}^{inter}\right] + \sum_{B \neq A} X_{AB}\Delta_{AB}^{intra} \tag{2}$$

X_0 is the monomer fraction (molecules with no bonded sites), which for the specific case, where only two sites (A and B) on a molecule can bond intramolecularly, is given by:

$$X_0 = X_A\left(1 + \rho \sum_B X_B\Delta_{AB}^{intra}\right) \tag{3}$$

X_{AB} is the fraction of molecules where both sites A and B are unbonded, which for the same specific case is given by:

$$X_{AB} = \frac{X_A}{1 + \rho \sum_C X_C\Delta_{BC}^{inter}} \tag{4}$$

Δ_{AB}^{inter} and Δ_{AB}^{intra} are the inter- and intramolecular association strengths, respectively. For sPC-SAFT, Δ_{AB}^{inter} is defined as:

$$\Delta_{AB}^{inter} = \frac{\pi}{6}\sigma^3 g^{HS}(d)\kappa^{AB}\left[\exp\left(\frac{\varepsilon^{AB}}{kT}\right) - 1\right] \tag{5}$$

where σ is the segment diameter, g^{HS} is the partial radial distribution function of hard spheres, and κ^{AB} and ε^{AB} are the association volume and energy, respectively. The expression for Δ_{AB}^{intra} used in this work was taken from Sear and Jackson.[14] They suggest setting the intramolecular association strength equal to the intermolecular association strength multiplied by W_n:

$$\Delta_{AB}^{intra} = W_n\Delta_{AB}^{intra} = W_n\frac{\pi}{6}\sigma^3 g^{HS}(d)\kappa^{AB}\left[\exp\left(\frac{\varepsilon^{AB}}{kT}\right) - 1\right] \tag{6}$$

where W_n is the value of the end-to-end distribution function of a freely jointed chain of n links, when the end links are the length of
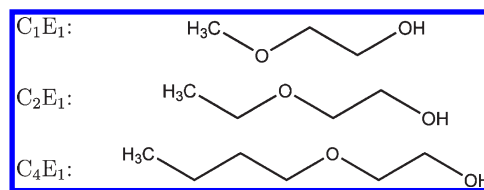

Figure 3. Structures of 2-methoxyethanol (C_1E_1), 2-ethoxyethanol (C_2E_1), and 2-butoxyethanol (C_4E_1).

one link apart. W_n is defined as:

$$W_n = \frac{n(n-1)}{\sigma^3 8\pi}\sum_{j=0}^{l}\frac{(-1)^j}{j!(n-j)!}\left[\frac{n-1-2j}{2}\right]^{n-2} \tag{7}$$

where l is the smallest integer satisfying:

$$l \geq \frac{n-1}{2} - 1 \tag{8}$$

(There was a misprint in the expression for W_n in the paper by Sear and Jackson, which has been corrected in eq 7.) The expression for the intramolecular association strength in eq 6 implies using identical association parameters for inter- and intramolecular association, which is an approximation, but also maintains the number of adjustable parameters. In this way, the new theory for intramolecular association can be compared to "normal" sPC-SAFT (without intramolecular association) with the same number of parameters, and thereby on equal terms.

■ RESULTS WITH SPC-SAFT

Association Scheme. There is consensus in the SAFT community of using the nomenclature for association schemes presented by Huang and Radosz,[16] but that nomenclature is not systematic. Instead, we use a nomenclature, where association schemes are defined by the total number of associating sites, x, the number of proton acceptor sites, y, and the number of proton donor sites, z, written as $x(y{:}z)$. This definition is identical to the one used by Yarrison and Chapman[17] and by Avlund et al.[18]

Three glycolethers have been considered in this work: 2-methoxyethanol (C_1E_1), 2-ethoxyethanol (C_2E_1), and 2-butoxyethanol (C_4E_1). The structures of the three glycol ethers are shown in Figure 3. The multifunctionality of glycol ethers gives the option of several association schemes, and different association schemes have been used for modeling glycol ethers with SAFT type theories in the literature; Garrido et al.[10] applied both the 2 (1:1) and the 3 (2:1) schemes, while Garcia-Lisbona et al.[11] used a complex scheme with three sites for each ether oxygen and three sites for the hydroxyl group, where some sites are only allowed to cross-associate, while others can self- as well as cross-associate. (The association scheme used by Garcia-Lisbona et al. is actually an implicit way of accounting for intramolecular association.) The 3 (2:1) scheme (one proton donor site and one proton acceptor site for the hydroxyl group and one proton acceptor site for the ether oxygen) is the simplest reasonable scheme for which intramolecular association is possible, and only this scheme is used in this work. A similar definition of the associating sites is used in the work with lattice theories for polyethoxyalcohols.[6−9]

Parameter Estimation. Two parameter sets have been estimated for each of the three glycol ethers: one set for regular sPC-SAFT,[12] and one for sPC-SAFT plus intramolecular association.

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Table 1. PC-SAFT Parameters for Three Glycol Ethers, Temperature Interval Used in the Parameter Estimation, and Average Relative Deviation (ARD%) between sPC-SAFT and DIPPR Correlations[19] in the Temperature Range of the Estimation

| | σ [Å] | ε [K] | m | ε^{AB} [K] | κ^{AB} | T [K] | ARD%[a] | |
							P^{sat}	V_m^L
C_1E_1 inter	2.958	187.69	3.956	1698.3	0.4975	282−508	2.31	0.21
C_1E_1 intra	2.779	187.97	4.768	1546.9	0.5603	310−508	1.71	0.30
C_2E_1 inter	2.999	189.56	4.693	1289.2	0.9179	285−512	2.28	0.24
C_2E_1 intra	2.921	187.95	5.055	1465.7	0.6375	313−512	1.74	0.28
C_4E_1 inter	3.518	257.63	4.194	1206.7	0.0446	317−571	0.39	0.23
C_4E_1 intra	3.252	203.41	5.127	1465.7	0.6375	317−571	4.18	0.18

[a] ARD% = $1/NP\Sigma|1 - \chi_i^{calc}/\chi_i^{exp}| \times 100\%$.

sPC-SAFT plus intramolecular association means that the new association term presented by Avlund et al.[5] (eq 1), where intramolecular association is included, is used instead of the usual association term from sPC-SAFT, while the remaining terms are the same for the two models. Using the expression for the intramolecular association strength in eq 6 from Sear and Jackson[14] enables us to use identical values of the association parameters for inter- and intramolecular association ($\varepsilon^{inter} = \varepsilon^{intra}$ and $\kappa^{inter} = \kappa^{intra}$). The two models therefore have the same five adjustable pure component parameters. The W_n parameter in eq 7 depends on the number of links (bonds), n, between the intramolecularly associating sites and on the segment diameter. The number of links between the ether oxygen and the hydroxyl hydrogen in the three glycol ethers considered here is 4, giving the following value of W_n:

$$W_4 = 0.0248/\sigma^3 \tag{9}$$

The pure component sPC-SAFT parameters were obtained by fitting DIPPR[19] correlations of pure component vapor pressure and liquid density. The parameters for the three glycol ethers are listed in Table 1. Inter indicates parameter sets for sPC-SAFT without intramolecular association (sPC-SAFT-inter), and intra indicates sets for sPC-SAFT plus intramolecular association (sPC-SAFT-intra).

When parameters were estimated for C_4E_1 by fitting pure component vapor pressure and liquid density in the temperature interval corresponding to $T_r = 0.5−0.9$, relatively small association parameters were obtained as compared to the other two glycol ethers, as seen for the inter parameter set in Table 1. The only difference between the two models used in this work is related to association, and the two models are therefore very similar if there is little association. Almost identical inter and intra parameters were therefore obtained, and the two parameter sets resulted in very similar results. A further discussion is presented in Chapter 6 of the Ph.D. thesis by Avlund.[4]

On the basis of the structures of the three glycol ethers, there is no reason why the association of C_4E_1 should be significantly weaker than for the other two glycol ethers, and a new intra parameter set was therefore estimated on the basis of the association parameters of C_2E_1. This procedure was decided on the basis of an observation of very similar association strengths for C_1E_1 and C_2E_1 for sPC-SAFT-intra. It should be noted that the error in vapor pressure with the intra parameters for C_4E_1 is around 4%, which is significantly higher than that for the other parameter
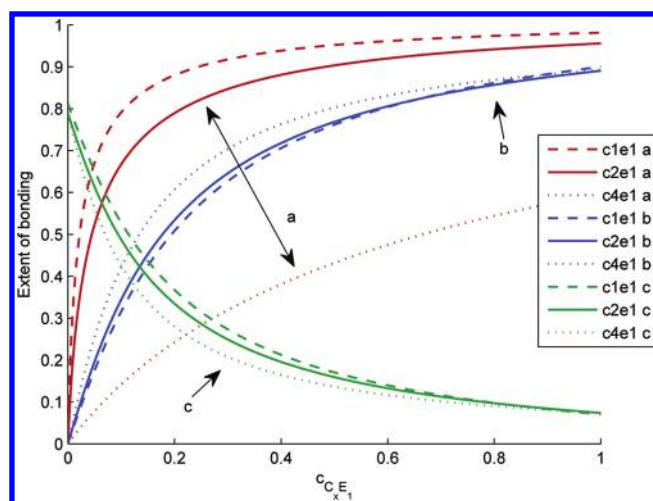

Figure 4. Amount of inter- and intramolecular bonds in C_xE_1−n-hexane. a = intermolecular association with inter parameters, b = intermolecular association with intra parameters, and c = intramolecular association with intra parameters.

sets, and which of course is dissatisfactory. The vapor pressure error with the inter parameters for C_4E_1 is surprisingly small as compared to the other sets, and the m parameter in that set is smaller than m in the inter set for C_2E_1, which of course does not make sense physically. (Because of the intercorrelation of the parameters, σ for the C_4E_1 inter set is accordingly considerably larger than for the other sets.) It would therefore be advantageous to reconsider the parameter estimation for C_4E_1, maybe in combination with the parameters for C_1E_1 and C_2E_1, but that is outside the scope of this work, and the presented parameters have been used for an initial investigation of C_4E_1.

The six parameter sets are compared by considering the amount of inter- and intramolecular bonds predicted in a mixture of C_xE_1 and n-hexane. The results are shown in Figure 4. The calculations were done for a single liquid phase at $P = 1.013$ bar and $T = 300$ K, with $k_{ij} = 0$.

As expected from the values of the association parameters, the inter parameters for C_4E_1 predict significantly less intermolecular association than do the other parameter sets. The amount of bonds predicted with the inter parameters for C_1E_1 and C_2E_1 differs somewhat, while the intra parameter sets for the three glycol ethers give rather similar results. For C_1E_1 and C_2E_1, sPC-SAFT-intra predicts less intermolecular association than does sPC-SAFT-inter, because of the competition from intramolecular association.

There are large uncertainties involved in the estimation of the amount of bonds with spectroscopy, and we have therefore decided not to make a quantitative comparison between sPC-SAFT and experimental data, but a qualitative comparison of Figures 2 and 4 shows that the results with sPC-SAFT-intra predict the same trends as the spectroscopic data show.

VLE and LLE Results for Self-Associating Mixtures. We first consider binary mixtures of glycol ethers and an inert (nonassociating) compound. The PC-SAFT parameters for the alkanes were taken from Gross and Sadowski.[20] Figures 5 and 6 show VLE and LLE results for C_1E_1−n-hexane. sPC-SAFT-inter does not predict ($k_{ij} = 0$) LLE for this system, whereas sPC-SAFT-intra predicts a too high upper critical solution temperature (UCST). It is not possible with either model to correlate (fitting a
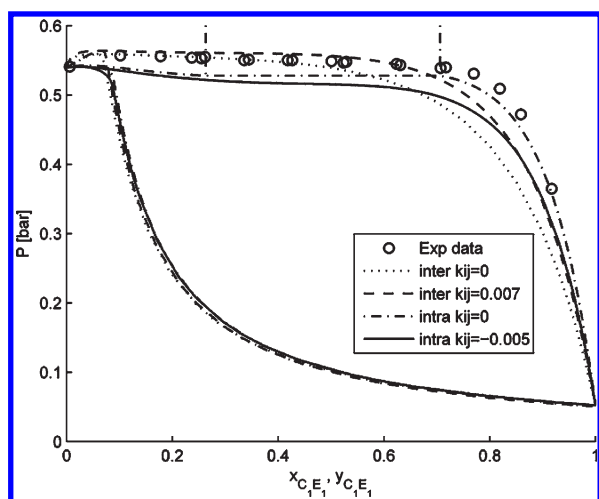
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Figure 5. C_1E_1−n-hexane VLE at T = 323.15 K. Experimental data: Dolch et al.[21]

Figure 6. C_1E_1−n-hexane LLE at P = 1.013 bar. Experimental data: Bijl et al.[22]

Figure 7. C_2E_1−n-octane VLE at P = 1.013 bar. Experimental data: Murti and Van Winkle.[23]
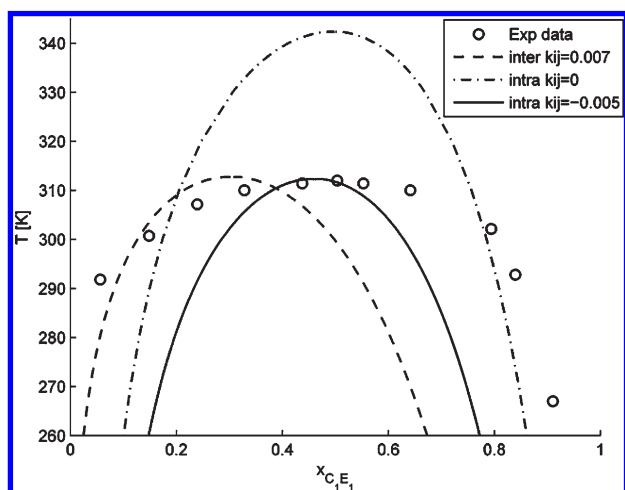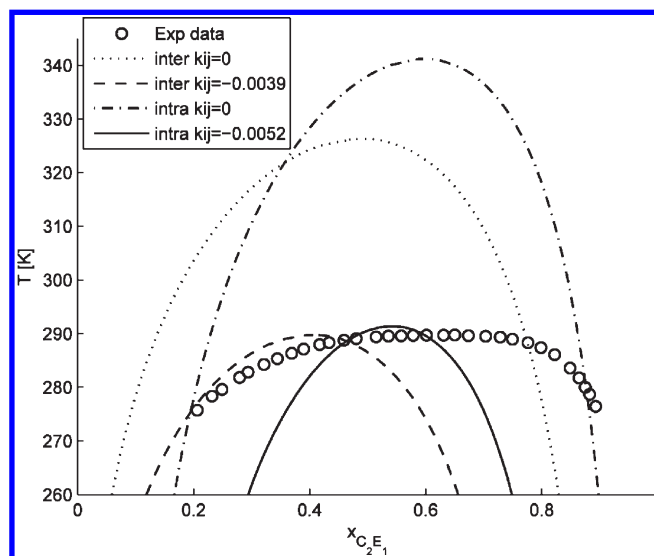

Figure 8. C_2E_1−n-dodecane LLE at P = 1.013 bar. Experimental data: Rubio et al.[24]

binary interaction parameter, k_{ij}) the very flat upper part of the immiscibility area. If the interaction parameter is fitted to match the UCST, the estimated immiscibility area becomes too small (narrow) with both models. The results with sPC-SAFT-intra deviate similarly for the two phases, while the results with sPC-SAFT-inter are shifted to lower glycol ether concentrations. There is only a small single phase temperature interval between the VLE and LLE data, and because sPC-SAFT-intra overestimates UCST it predicts VLLE at T = 323.15 K.

The same k_{ij} values are used for VLE and LLE for C_1E_1−n-hexane, but it is not possible to match all of the VLE data points with either model even with a k_{ij} optimized for VLE. sPC-SAFT-inter can only match the data points at medium and low glycol ether concentrations, while sPC-SAFT-intra matches the glycol ether rich part well, but is disturbed by the model prediction of LLE at lower concentrations. Similar results are obtained for C_1E_1−n-heptane.

VLE results are shown for C_2E_1−n-octane in Figure 7. sPC-SAFT-inter and sPC-SAFT-intra both predict the azeotrope of this mixture, although both models slightly underpredict the azeotrope temperature. The error with sPC-SAFT-inter is twice
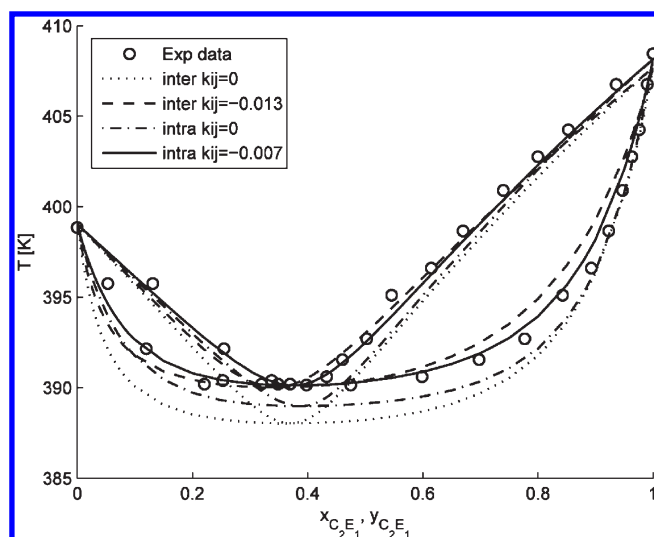
the error with sPC-SAFT-intra. It is possible with both models to correlate the data including the azeotrope satisfactorily by fitting a k_{ij}, although slightly better results are obtained with sPC-SAFT-intra than with sPC-SAFT-inter.

Figure 8 shows the LLE results for C_2E_1−n-dodecane. Both models predict LLE for this system, and both overestimate the UCST. The results with an interaction parameter fitted to match UCST are similar to the results for C_1E_1−n-hexane. The estimated immiscibility areas are too narrow, and the sPC-SAFT-inter results are shifted toward lower glycol ether concentrations as compared to the sPC-SAFT-intra results, which lie in the center of the experimental immiscibility area.

The results for C_4E_1−n-octane are shown in Figure 9. Here, sPC-SAFT-intra gives significantly better results for k_{ij} = 0, and a better match to the liquid curve with an optimal k_{ij} than sPC-SAFT-inter. sPC-SAFT-inter correlates the vapor curve slightly
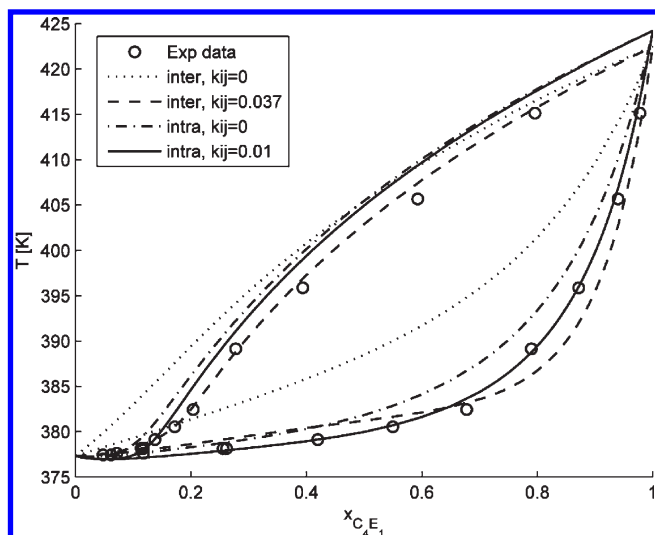
Figure 9. C_4E_1–n-octane VLE at $P = 0.533$ bar. Experimental data: Komatsu et al.[25]
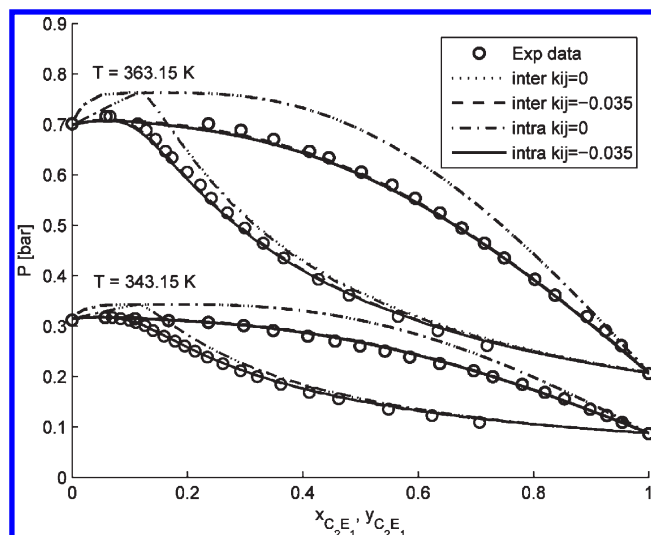

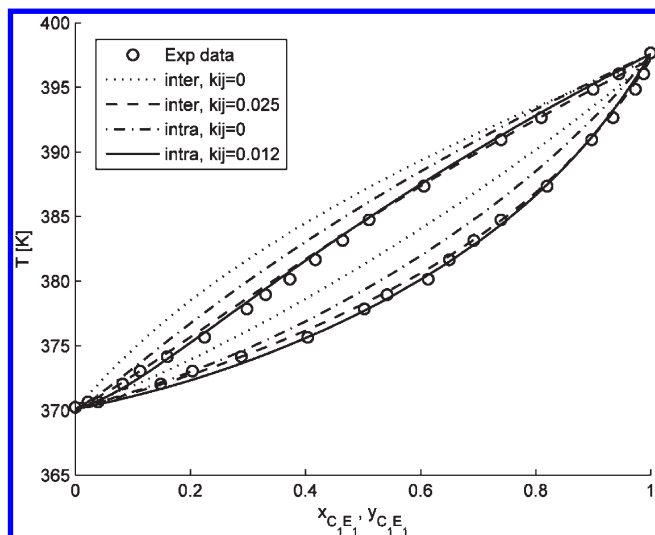**Figure 11.** C_2E_1–water VLE at $T = 343.15$ and 363.15 K. Experimental data: Chiavone-Filho et al.[30]

Figure 10. C_1E_1–propanol VLE at $P = 1.013$ bar. Experimental data: Chandak et al.[28]
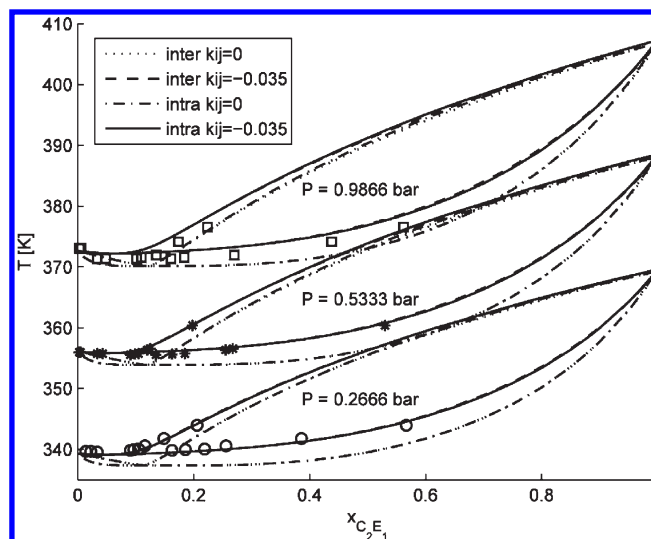

Figure 12. C_2E_1–water VLE at $P = 0.2666$, 0.5333, and 0.9866 bar. Experimental data: Boublik and Kuchynka.[31]

better than sPC-SAFT-intra, which is a result of the large error in vapor pressure for pure C_4E_1 with sPC-SAFT-intra.

VLE and LLE Results for Cross-Associating Mixtures. Next, we consider binary mixtures of glycol ethers with other associating compounds. The Elliott combining rule[26] was used in the calculations.

Figure 10 shows the results for C_1E_1–propanol with $k_{ij} = 0$ as well as with fitted k_{ij}. Propanol was modeled using the 2 (1:1) scheme and generalized alkanol parameters from Grenner et al.[27] sPC-SAFT-intra gives a better prediction for this mixture than does sPC-SAFT-inter, but the cross-attractions between the two compounds are overestimated by both models. Both models correlate the system very satisfactorily with a small positive k_{ij}. sPC-SAFT-inter needs a larger k_{ij} than sPC-SAFT-intra because of the larger error in the predictions.

The results for C_2E_1–water are shown in Figures 11 and 12. Water was modeled with the 4 (2:2) scheme and the parameters from Grenner et al.[29] The figures show the results with both

sPC-SAFT-inter and sPC-SAFT-intra, but the results with the two models are indistinguishable. As seen from the figures, sPC-SAFT very satisfactorily models this system, and a single k_{ij} is sufficient to match the experimental data, including the azeotrope, at all temperatures and pressures investigated here.

The last cross-associating mixture with a glycol ether to be considered here is C_4E_1–water. This is a very interesting mixture, both because of its industrial applications and because it exhibits closed-loop LLE. The closed-loop LLE is a result of the competition between energetic and entropic effects. At temperatures above UCST, the system will minimize its free energy by maximizing its compositional and orientational entropy. At intermediate temperatures, the entropy is less important, and the system will consequently try to minimize the enthalpy. The system will therefore split into two immiscible liquid phases because of the weak van der Waals forces between unlike molecules. At temperatures below the lower critical solution
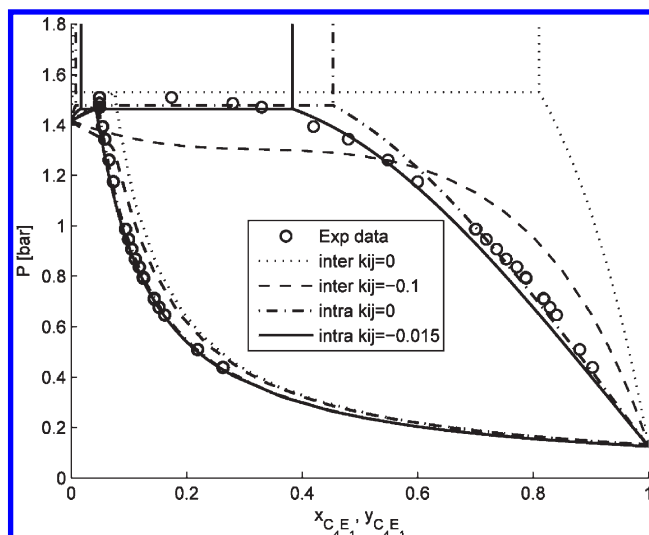
Figure 13. C_4E_1—water VLE at $T = 383.15$ K. Experimental data: Schneider and Wilhelm.[32]
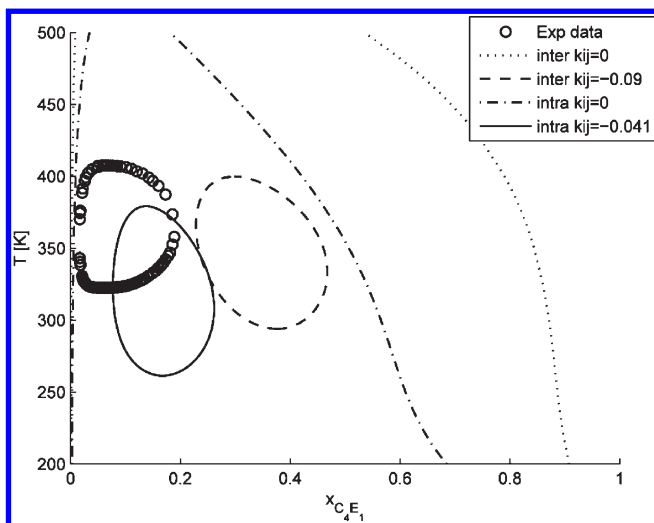

Figure 14. C_4E_1—water LLE at $P = 10.13$ bar. Experimental data: Aizpiri et al.[33]

Figure 15. Results with sPC-SAFT-inter for C_4E_1—water LLE at $P = 10$, 200, and 600 atm. Experimental data: Schneider,[34] taken from Knudsen et al.;[35] 10 atm ($*$), 200 atm ($\diamond$), and 600 atm ($\square$).

temperature (LCST), cross-association becomes strong enough to overcome the unfavorable enthalpy and orientational entropy and to keep the mixture in one phase.[11] Because the entropic effects are essential for the formation of closed-loop LLE, the highly anisotropic hydrogen bonds must be treated in the theory to describe the phase behavior. An EoS like sPC-SAFT is therefore in theory capable of modeling closed-loop LLE.

Figure 13 shows the VLE results and Figure 14 the LLE results with sPC-SAFT for this mixture. sPC-SAFT-intra gives significantly better VLE results for this mixture than does sPC-SAFT-inter, but the predicted VLLE area is in both cases larger than what the experimental data suggest, which disturbs the results for the liquid curve. It is not possible to fit a k_{ij} to match the entire liquid curve.

Neither of the models are capable of correlating the data points for the closed-loop LLE of this mixture. Both models significantly overestimate the immiscibility area both in temperature and composition, and fitting one interaction parameter is not enough
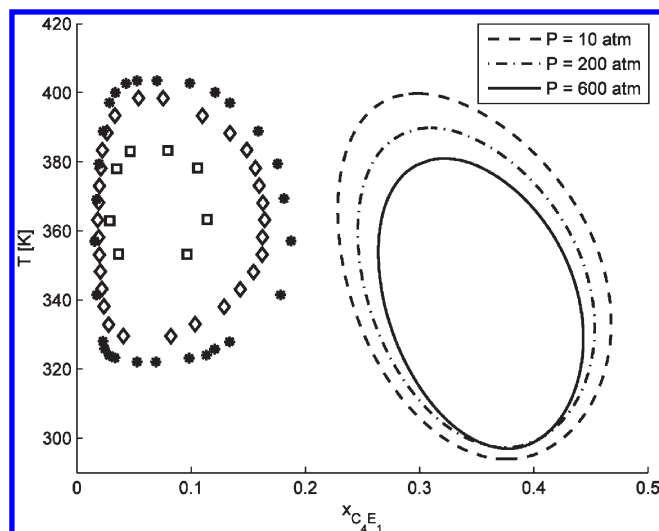
to match the experimental data points. It is possible with sPC-SAFT-inter to get a good match of UCST and LCST with the same k_{ij}, but then the composition of the water-rich phase is overestimated with an order of magnitude. sPC-SAFT-intra gives a significantly better correlation of the composition than does sPC-SAFT-inter, but UCST and LCST are not as well matched as with sPC-SAFT-inter. (The k_{ij} values for LLE were fitted to give an immiscibility area of approximately the same size as the experimental data shows). The fact that sPC-SAFT-inter predicts a significantly larger immiscibility area than what the experimental data show could be a result of the weak association with the C_4E_1 inter parameters, because more cross-association presumably will increase the miscibility between C_4E_1 and water. This was part of the reasoning behind the new intra parameter set, and it is clear from Figures 13 and 14 that stronger association has improved the results, even though the immiscibility area predicted with sPC-SAFT-intra is also significantly larger than what the experimental data suggest.

Among the applications of glycol ethers in the petroleum industry is enhanced oil recovery (EOR) by chemical flooding of the oil reservoirs. Because the reservoir pressures are usually significantly higher than atmospheric pressure, it is important to know how the efficiency of the flooding depends on pressure. As a step in that investigation, it is also of importance to know how the miscibility of C_4E_1 and water is influenced by pressure. Schneider[34] has presented extrapolated LLE data for this mixture at different pressures. Figures 15 and 16 show the results with sPC-SAFT-inter and sPC-SAFT-intra, respectively, at $P = 10$, 200, and 600 atm.

sPC-SAFT-inter predicts qualitatively the correct pressure dependency, but the experimental data show a stronger pressure dependency than what is predicted with the model. Moreover, the predicted LLE area shifts toward lower temperatures as the pressure increases, as compared to the experimental data.

sPC-SAFT-intra gives a better prediction of the pressure dependency than does sPC-SAFT-inter. Where sPC-SAFT-inter gives a weaker pressure dependency than the experimental data show, the pressure dependency of sPC-SAFT-intra for C_4E_1 is very similar to the experimental pressure dependency.
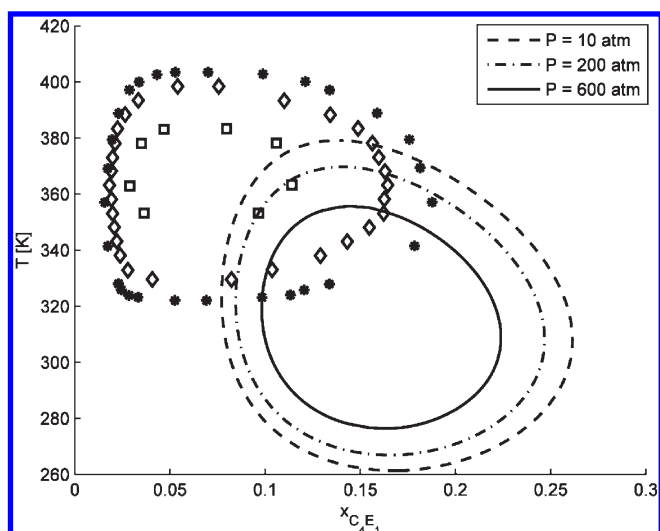
Figure 16. Results with sPC-SAFT-intra for C_4E_1—water LLE at $P = 10$, 200, and 600 atm. Experimental data: Schneider,[34] taken from Knudsen et al.;[35] 10 atm ($*$), 200 atm ($\diamond$), and 600 atm ($\square$).

It is important to note that the difference in the results with sPC-SAFT-inter and sPC-SAFT-intra for C_4E_1 is mainly a result of the different parameter estimation procedures. Estimating a new parameter set for sPC-SAFT-intra with stronger association significantly improved the results (the original parameter set gave results almost identical to the ones presented for sPC-SAFT-inter), confirming that the parameters obtained from pure C_4E_1 data underestimated the association. On the basis of this observation, it is believed that better parameters can also be obtained for sPC-SAFT-inter, if stronger association is enforced. On the basis of the results with sPC-SAFT-intra presented here, it is believed that if a parameter set was fitted to match the experimental LLE data points at $P = 1$ bar, then sPC-SAFT-intra could predict the data points at higher pressures. This has not been investigated in this work.

COMPARISON WITH OTHER ASSOCIATION MODELS

The results presented for glycol ethers with lattice theories in the literature are mainly for excess enthalpies, and phase equilibrium for mixtures with CO_2, and it is therefore not possible to compare the two approaches presented in this work.

Garrido et al.,[10] on the other hand, considered many of the same systems that were investigated here. They interestingly found that 2 sites for glycol ethers in most cases gave better results than 3 sites, and a comparison shows that the 2 (1:1) results with CPA are very similar to the results with 3 (2:1) with sPC-SAFT-inter. The only system where that is not the case is C_4E_1—water. Here, Garrido et al. found that the 2 (1:1) scheme gives good results for VLE, and the 3 (2:1) scheme gives good results for LLE, and the results are in both cases significantly better than the results obtained with sPC-SAFT, whether intramolecular association is included or not. It is not possible with CPA to obtain good results for both VLE and LLE with the same association scheme for this mixture.

The closed-loop LLE of C_4E_1—water was also investigated by Garcia-Lisbona et al.,[11] who found it necessary to fit the number and type of associating sites, as well as the parameters to the LLE data to match the experimental data points. With parameters and

an association scheme obtained in this way, they get LLE results similar to the 2 (1:1) CPA results. Reasonable VLE results were obtained using the k_{ij} fitted for LLE.

CONCLUSION

sPC-SAFT was in general found to perform satisfactorily for glycol ether-containing mixtures, both with and without the new theory for intramolecular association. The predicted results are in most cases better when intramolecular association is included, especially for LLE, while similar results were obtained with a fitted binary interaction parameter. sPC-SAFT was in general found to give very good results for miscible mixtures and reasonably good results for immiscible mixtures, except for the mixture of C_4E_1—water, for which the results were not satisfactory.

On the basis of the very similar association strengths for C_1E_1 and C_2E_1 with sPC-SAFT-intra, a new parameter set was estimated for C_4E_1 with the association parameters from C_2E_1. With these parameters, sPC-SAFT-intra was found to give significantly better VLE results for C_4E_1—water, as well as better LLE results than sPC-SAFT-inter. This difference between sPC-SAFT-inter and sPC-SAFT-intra for C_4E_1 is, however, mainly caused by the difference in the parameter estimation, and not by the difference in the theories. The five adjustable parameters may have a larger influence on the performance of the model than improvements in the theory (at least for this type of calculations), which explains the similar results obtained in this work with sPC-SAFT with and without intramolecular association. There is thus no significant gain in using the new, more extensive theory for this kind of calculations, but the new theory is expected to be of more importance for other types of calculations, including derivative properties, multicomponent mixtures, and group contribution methods for multifunctional compounds. If, for example, the parameters for hydroxyl and amine groups are estimated for alcohols and amines, and applied for glycols and alkanolamines, then the effects that are only present for multifunctional compounds, like intramolecular association, must be accounted for.

A comparison between sPC-SAFT-inter and CPA showed that the results with sPC-SAFT (without intramolecular association) with the 3 (2:1) scheme and CPA with the 2 (1:1) scheme are similar.

APPENDIX: DERIVATIVES OF THE HELMHOLTZ FREE ENERGY

This Appendix will present expressions for the derivatives of the Helmholtz free energy needed to calculate pressure and chemical potential for the theory for intramolecular association presented by Avlund et al.[5] Michelsen and Hendriks[36] presented a simple way to calculate these derivatives when only intermolecular association is considered, and the same approach is used here. The derivatives are given for the case where only two sites on a molecule can associate intramolecularly.

The nomenclature used in this Appendix is convenient for programming, because it reduces the number of sums, as compared to the normal SAFT nomenclature. All sites in the system are listed after each other, starting with the sites on component 1, followed by the sites on component 2, and so on. Sites are referred to by the number in the list. XA_i is thus the fraction of sites i not bonded, and XAB_{ij} is the fraction of molecules where both sites i and j are not bonded. x_k is the component mole fraction, while x_i is the mole fraction of site i,

which is equal to the mole fraction of the component, which site i belongs to, multiplied by the repetition factor of the site. Sums over i and j are implicitly over all sites in the system if not otherwise stated, except for intramolecular interactions, where sums over j implicitly are understood only to be a sum over sites on the same molecule as site i, because the two sites involved in an intramolecular bond must belong to the same molecule.

The intermolecular association strength is per mole, and for sPC-SAFT the expressions for Δ^{inter} and W_n in eqs 5 and 7 must therefore be corrected with Avogadro's number.

The starting point is the function Q, which is equal to the Helmholtz free energy at the stationary point with respect to the site fractions X, given by:

$$Q/n = \sum_k^{NC} x_k (\ln X0_k + K_k + 1 - \sum_i^{NS_k} XA_i)$$

$$-\frac{1}{2V_m} \sum_i \sum_j x_i x_j XA_i XA_j \Delta_{ij}^{\text{inter}} - \frac{1}{2} \sum_i \sum_{j \neq i} x_i XAB_{ij} \Delta_{ij}^{\text{intra}}$$

$$(10)$$

with

$$K_k = X0_k \sum_{P(\Gamma_k) = \{\gamma, M \geq 2\}} (-1)^M (M-2)! \prod_{\gamma_k} \frac{X_{\Gamma_k - \gamma_k}}{X0_k}$$

$$(11)$$

$X0_k$ is the monomer fraction of component k, NC is the number of components, and NS_k is the number of sites on component k.

The Q function has the property that all derivatives with respect to any bonding state, X_α, are zero:

$$\frac{\partial Q}{\partial X_\alpha} = 0 \qquad (12)$$

and in the stationary point:

$$Q_{sp} = \frac{A^{\text{assoc}}}{RT} = \sum_k^{NC} x_k \left(\ln X0_k - \sum_i^{NS_k} (XA_i - 1) \right)$$

$$-\frac{1}{2} \sum_i \sum_{j \neq i} x_i XAB_{ij} \Delta_{ij}^{\text{intra}} \qquad (13)$$

$$-1 + XA_i \left[1 + \frac{1}{V_m} \sum_j x_j XA_j \Delta_{ij}^{\text{inter}} \right] + \sum_{j \neq i} XAB_{ij} \Delta_{ij}^{\text{intra}} = 0$$

$$(14)$$

and

$$K_k = -1 + \sum_i^{NS_k} XA_i - \frac{n}{V} \sum_i^{NS_k} \sum_j x_j XA_i XA_j \Delta_{ij}^{\text{inter}}$$

$$-\frac{1}{2} \sum_i^{NS_k} \sum_{j \neq i} XAB_{ij} \Delta_{ij}^{\text{intra}} \qquad (15)$$

The derivation of eqs 13—15 is shown in the paper by Avlund et al.[5]

The pressure is obtained from the volume derivative of the Helmholtz free energy:

$$\frac{P^{\text{assoc}}}{RT} = -\frac{\partial Q_{sp}}{\partial V} \qquad (16)$$

The derivative of Q is calculated using the chain rule:[36]

$$\frac{\partial Q_{sp}}{\partial V} = \left(\frac{\partial Q}{\partial V} \right)_X + \sum_k \sum_{\alpha \subset \Gamma_k} \frac{\partial Q}{\partial X_\alpha} \frac{\partial X_\alpha}{\partial V} = \left(\frac{\partial Q}{\partial V} \right)_X \qquad (17)$$

and thus

$$-\frac{P^{\text{assoc}}}{RT} = \frac{-n^2}{2V} \left(-\frac{1}{V} \sum_i \sum_j x_i x_j XA_i XA_j \Delta_{ij}^{\text{inter}} \right.$$

$$\left. + \sum_i \sum_j x_i x_j XA_i XA_j \frac{\partial \Delta_{ij}^{\text{inter}}}{\partial V} \right) - \frac{n}{2} \sum_i \sum_j x_i XAB_{ij} \frac{\partial \Delta_{ij}^{\text{intra}}}{\partial V}$$

$$(18)$$

Δ^{inter} and Δ^{intra} only depend on volume (and composition) through the radial distribution function g. The volume derivative of Δ^{inter} is:

$$\frac{\partial \Delta^{\text{inter}}}{\partial V} = \frac{\Delta^{\text{inter}}}{g} \frac{\partial g}{\partial V} = \Delta^{\text{inter}} \frac{\partial \ln g}{\partial V} \qquad (19)$$

and similarly for Δ^{intra}. Using this and eq 14, we can simplify the expression for the pressure:

$$-\frac{P^{\text{assoc}}}{RT} = \frac{n^2}{2V^2} \sum_i \sum_j x_i x_j XA_i XA_j \Delta_{ij}^{\text{inter}}$$

$$-\left(\frac{n^2}{2V} \sum_i \sum_j x_i x_j XA_i XA_j \Delta_{ij}^{\text{inter}} + \frac{n}{2} \sum_i \sum_j x_i XAB_{ij} \Delta_{ij}^{\text{intra}} \right)$$

$$\times \frac{\partial \ln g}{\partial V} = \frac{n^2}{2V^2} \sum_i \sum_j x_i x_j XA_i XA_j \Delta_{ij}$$

$$-\frac{n}{2} \sum_i x_i (1 - XA_i) \frac{\partial \ln g}{\partial V} \qquad (20)$$

The chemical potential of component l is obtained from the compositional derivative of the Helmholtz free energy:

$$\frac{\mu_l^{\text{assoc}}}{RT} = \frac{\partial Q_{sp}}{\partial n_l} = \left(\frac{\partial Q}{\partial n_l} \right)_X + \sum_k \sum_{\alpha \subset \Gamma_k} \frac{\partial Q}{\partial X_\alpha} \frac{\partial X_\alpha}{\partial n_l} = \left(\frac{\partial Q}{\partial n_l} \right)_X \qquad (21)$$

We have to distinguish between associating and nonassociating components. For nonassociating components, we find:

$$\frac{\mu_l^{\text{assoc}}}{RT} = -\left(\frac{n^2}{2V} \sum_i \sum_j x_i x_j XA_i XA_j \Delta_{ij}^{\text{inter}} + \frac{n}{2} \sum_i \sum_{j \neq i} x_i XAB_{ij} \Delta_{ij}^{\text{intra}} \right) \frac{\partial \ln g}{\partial n_l}$$

$$= -\frac{n}{2} \sum_i x_i (1 - XA_i) \frac{\partial \ln g}{\partial n_l} \qquad (22)$$

and for associating components we have:

$$\frac{\mu_l^{\text{assoc}}}{RT} = \ln X0_l$$

$$+ \left[1 + K_l - \sum_i^{NS_l} XA_i - \frac{n}{V} \sum_i^{NS_l} \sum_j x_j XA_i XA_j \Delta_{ij}^{\text{inter}} - \frac{1}{2} \sum_i^{NS_k} \sum_{j \neq i} XAB_{ij} \Delta_{ij}^{\text{intra}} \right]$$

$$- \left(\frac{n^2}{2V} \sum_i \sum_j x_i x_j XA_i XA_j \Delta_{ij}^{\text{inter}} + \frac{n}{2} \sum_i \sum_{j \neq i} x_i XAB_{ij} \Delta_{ij}^{\text{intra}} \right) \frac{\partial \ln g}{\partial n_l}$$

$$= \ln X0_l - \frac{n}{2} \sum_i x_i (1 - XA_i) \frac{\partial \ln g}{\partial n_l} \qquad (23)$$

The terms in the square bracket sum to zero according to eq 15, and $\ln X0_l$ is the only difference between the derivative for associating and nonassociating components.

More derivatives are given in the Ph.D. thesis by Avlund.[4]

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