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Abstract

Goal of this work is the extension of a Perturbed-Hard-Sphere-Chain equation of state (PHSC EOS) to systems containing strong polar components. Three different types of association models (ten Brinke / Karasz, SAFT, modified Veytsman) were used to calculate the contribution of specific interactions like hydrogen bonding to thermodynamic quantities. Pure component parameters obtained from regression of temperature dependent density and vapor pressure data allow the prediction of VLE and LLE data. The results of simple fluids and polymer solutions were compared with experimental data. The SAFT and the modified Veytsman extension give similar results for pure fluids and mixtures with components of similar segment size. Differences increase with increasing difference of segment size.

1. Introduction

Goal of this work is the extension of the Perturbed-Hard-Sphere-Chain equation of state (PHSC EOS) developed by Song et al. [1994a, 1994b, 1994c] to systems containing strong polar components. This extension requires an additional term for specific interactions like hydrogen bonding.

$$A = A_{PHSC} + A_{assoc.} \tag{1.1}$$

$$Z = Z_{PHSC} + Z_{assoc.} \tag{1.2}$$

A : Helmholtz energy
Z : compressibility factor
PHSC : Perturbed Hard-Sphere-Chain
assoc. : association (specific interactions)

Three different types of association models have been tested to determine the best combination of Perturbed-Hard-Sphere-Chain equation of state and association model.

- ten Brinke / Karasz
- SAFT
- modified Veytsman

2. PHSC - theory

In PHSC theory, compressibility factor Z consists of four parts. The first part is due to the ideal gas, the second includes the hard sphere effect. Larger molecules are described as chain-like molecules consisting of several connected spheres. The influence of the sphere connectivity is taken into consideration by the third part. Attractive interactions are included by a van der Waals type perturbation term.

$$Z_{PHSC} = \frac{P}{\rho kT} = 1 + \rho \sum_{ij} x_i x_j r_i r_j b_{ij} g_{ij}(d_{ij}) - \sum_i x_i (r_i - 1)[g_{ii}(d_{ii}) - 1] - \frac{\rho}{kT} \sum_{ij} x_i x_j r_i r_j a_{ij} \tag{2.1}$$

where

P : pressure
$\rho = \frac{N}{V}$: molecular density
k : Boltzmann constant

T : absolute temperature

$x_i = \dfrac{N_i}{\sum_k N_k}$: mole fraction

r_i : chain length

b_{ij} : size parameter

$g_{ij}\left(d_{ij}\right)$: distribution function at contact

a_{ij} : attractive interaction parameter

$$b_{ij}(T) = \frac{2\pi}{3}\sigma_{ij}^3 \mathscr{F}_{b,ij}\left(kT/\varepsilon_{ij}\right) \qquad 2.2$$

$$a_{ij}(T) = \frac{2\pi}{3}\sigma_{ij}^3 \varepsilon_{ij} \mathscr{F}_{a,ij}\left(kT/\varepsilon_{ij}\right) \qquad 2.3$$

σ_{ij} : hard-sphere diameter

$\mathscr{F}_{a,ij}$, $\mathscr{F}_{b,ij}$: universal function for temperature dependence

ε_{ij} : interaction energy

$$\mathscr{F}_{a,ij}\left(kT/\varepsilon_{ij}\right) = \alpha_1 e^{-\alpha_2 (kT/\varepsilon_{ij})} + \alpha_3 e^{-\alpha_4 (kT/\varepsilon_{ij})^{3/2}} \qquad 2.4$$

$$\mathscr{F}_{b,ij}\left(kT/\varepsilon_{ij}\right) = \beta_1 e^{-\beta_2 (kT/\varepsilon_{ij})^{1/2}} + \left(1-\beta_1\right) e^{-\beta_3 (kT/\varepsilon_{ij})^{3/2}} \qquad 2.5$$

α_1	1.8681	β_1	0.7303
α_2	0.0619	β_2	0.1649
α_3	0.6715	β_3	2.3973
α_4	1.7317		

$$g_{ij} = \frac{1}{1-\eta} + \frac{3}{2}\frac{\zeta_{ij}}{(1-\eta)^2} + \frac{1}{2}\frac{\zeta_{ij}^2}{(1-\eta)^3} \qquad 2.6$$

$$\eta = \frac{\rho}{4}\sum_i x_i \cdot r_i \cdot b_{ii} \qquad 2.7$$

$$\zeta_{ij} = \left(\frac{b_{ii} \cdot b_{jj}}{b_{ij}}\right)^{1/3} \frac{\rho}{4}\sum_i x_i \cdot r_i \cdot b_{ii}^{2/3} \qquad 2.8$$

η : segment packing fraction

ζ_{ij} : reduced density

combining rules

$$\sigma_{ij} = \frac{1}{2}\left(\sigma_{ii} + \sigma_{jj}\right) \cdot \left(1 - l_{ij}\right) \qquad 2.9$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii} \cdot \varepsilon_{jj}} \cdot (1 - k_{ij}) \qquad 2.10$$

3. ten Brinke / Karasz - model

The ten Brinke / Karasz model [ten Brinke and Karasz (1984); Hino et al. (1993)] distinguishes between non-specific and specific interactions. Assuming that every molecule has several contact points, each contact point interacts with a contact point of a neighboring molecule in a non-specific way with the interaction energy ε_{ij}. Functional groups which are able to form specific interactions like hydrogen bonding are usually restricted to a small part of the molecule. Therefore, only certain contact points are able to interact in a specific way. To form a hydrogen bond two "specific" contact sites have to be in close spatial proximity because hydrogen bonds are short-range and highly oriented interactions.

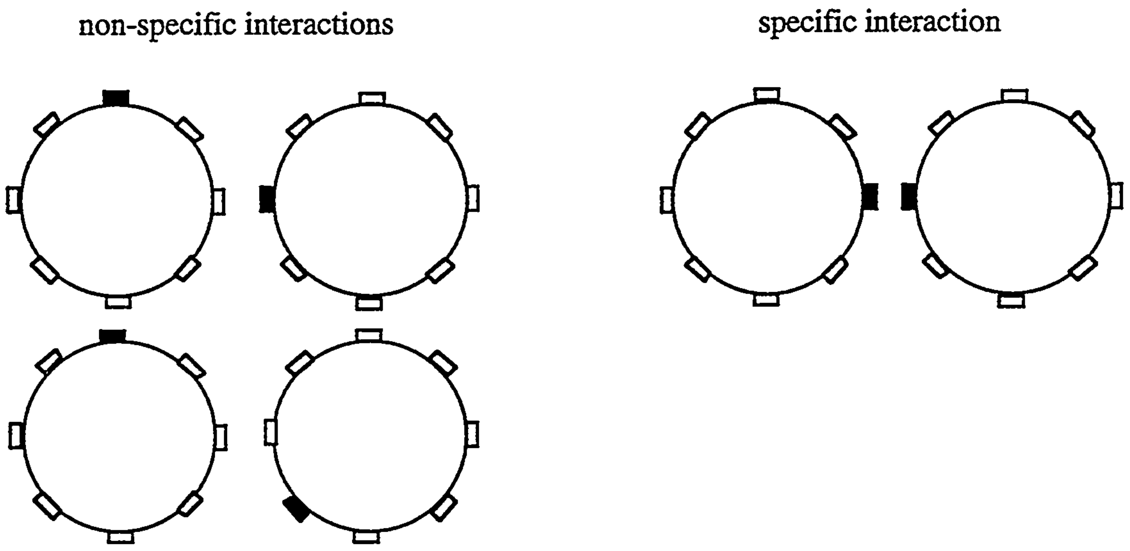


Figure 3.1 The ten Brinke / Karasz model distinguishes between non-specific and specific interactions.

The fraction of contact points f_{ij} which interact in a specific way is given by a Boltzmann distribution.

$$f_{ij} = \frac{1}{1 + \omega_{ij} \exp\left(E^0_{ij} / kT \right)} \qquad 3.1$$

f_{ij} : fraction of interactions which are specific interactions

ω_{ij} : degeneracy factor and entropic penalty
E_{ij}^0 : energy of specific interactions beyond that for nonspecific interactions

$$U_{assoc.} = \sum_i \sum_j \frac{1}{2} \cdot N_{ij} \cdot f_{ij} \cdot E_{ij}^0 = \sum_{ij} N_{ij} \cdot f_{ij} \cdot E_{ij}^0 \tag{3.2}$$

$N_{ij} = N \cdot x_i x_j r_i r_j$: number of ij contacts (s. perturbation term PHSC-theory)

The contribution to the Helmholtz energy can be calculated by integration with respect to reciprocal temperature.

$$\begin{aligned} A_{assoc.} &= \int_0^{1/T} \sum_{ij} N_{ij} \cdot f_{ij} \cdot E_{ij}^0 \, d\left(\tfrac{1}{T}\right) \\ &= \sum_{ij} N_{ij} \cdot \left[E_{ij}^0 - kT \cdot \ln\left(\frac{\omega_{ij} \exp\left(E_{ij}^0 / kT\right) + 1}{\omega_{ij} + 1} \right) \right] \end{aligned} \tag{3.3}$$

$$P_{assoc.} = -\left(\frac{\partial A_{assoc.}}{\partial V} \right)_{all\,N_i,T} = -\rho \cdot x_i x_j r_i r_j \cdot \left[E_{ij}^0 - kT \cdot \ln\left(\frac{\omega_{ij} \exp\left(E_{ij}^0 / kT\right) + 1}{\omega_{ij} + 1} \right) \right] \tag{3.4}$$

$$Z_{assoc.} = \frac{P_{assoc.}}{\rho kT} \tag{3.5}$$

4. SAFT - model

The SAFT model (Statistical Association Fluid Theory) [Wertheim (1984a,b), (1986a-c), Chapman et al. (1989), (1990); Huang and Radosz (1990), (1991)] is based on the following assumptions. Hydrogen bonds are known as short-range, highly oriented interactions. A square-well potential is used to describe these attractive interactions. Because of the high orientation, bonding between two interaction sites A and B (see figure 4.1) can only occur, when the angle Θ_i between vector iA (vector connecting segment center i and association site A) and segment center connection line $\vec{r}_{ij}$ is smaller than a critical angle Θ_C. The same condition has to be fulfilled for the angle Θ_j between vector jB and the line connecting segment centers.

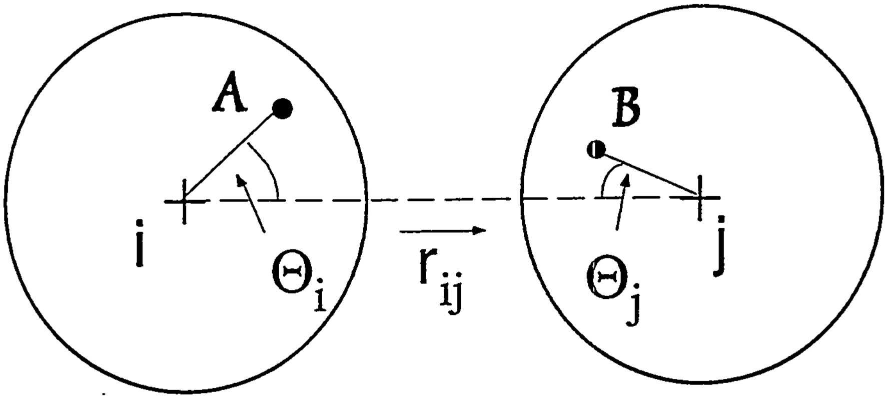


Figure 4.1 Hydrogen bonding requires a certain orientation between two association sites A and B ($\Theta_i < \Theta_c$ and $\Theta_j < \Theta_c$)

In addition, some steric factors are taken into account; these factors exclude the following cases from forming a hydrogen bond :

a) bonding of more than two molecules at a single site

b) simultaneously bonding of one site to two sites on another molecule

c) double bonding between molecules. This restriction can be relaxed [Wertheim (1986a-c)].

The expression for the Helmholtz energy was derived by Wertheim.

$$\frac{a_{\text{assoc.}}}{RT} = \sum_{i=1}^{n} x_i \left[\sum_{A_i}^{m} \left(\ln X^{A_i} - \frac{X^{A_i}}{2} \right) + \frac{1}{2} M_i \right] \qquad 4.1$$

$x_i = n_i \Big/ \sum_k n_k$: mole fraction of component i

$X^{A_i} = n_i^{\text{not bonded to } A} / n_i$: fraction of component i which is not bonded to association site *A*

$X^{B_j} = n_j^{\text{not bonded to } B} / n_j$: fraction of component j which is not bonded to association site *B*

n_i : moles of component i

M_i : total number of association sites on molecule i

$$X^{A_i} = \left[1 + \sum_{j=1}^{n} \sum_{B_j}^{m} \rho_j X^{B_j} \Delta^{A_i B_j} \right]^{-1} \qquad 4.2$$

$\rho_j = x_j \rho$: molecular density of component j

$\Delta^{A_iB_j}$: association strength

$$\Delta^{A_iB_j} \cong \sigma_{ij}^{3}\, \kappa_{A_iB_j}\, g(d_{ij}) \left[\exp\left(\frac{E^0_{A_iB_j}}{kT} \right) - 1 \right] \qquad 4.3$$

$E^0_{A_iB_j}$: association energy

$\kappa_{A_iB_j}$: bonding - site overlap volume element

$E^0_{A_iB_j}$ and $\kappa_{A_iB_j}$: adjustable parameters

Expressions for the chemical potential μ_K and the pressure P are given in appendix A.

$$\mu_k^{assoc.} = \left(\frac{\partial A_{assoc.}}{\partial N_k} \right)_{all\, N_i, V, T} \qquad 4.4$$

$$P = -\left(\frac{\partial A_{assoc}}{\partial V} \right)_{all\, N_i, T} \qquad 4.5$$

5. Veytsman - model

The derivation of this model [Veytsman (1990); Panayiotou and Sanchez (1991)] is based on the calculation of the partition function $Q_{assoc.}$ due to hydrogen bonding. Knowing the partition function Q yields the Helmholtz energy by using the general expression

$$A = k \cdot T \cdot \ln Q \qquad 5.1$$

or in the special case for hydrogen bonding

$$A_{assoc.} = k \cdot T \cdot \ln Q_{assoc.} \qquad 5.2$$

Q : partition function

$Q_{assoc.}$: partition function due to hydrogen bonding

The partition function $Q_{assoc.}$ can be calculated by counting all possible distributions of N_{ij} hydrogen bonds among N_i donor groups and N_j acceptor groups. Considering a mixture of t components with different kinds of donor groups, the total number of donor groups of type i (respectively acceptor groups j).is given by the summation over all components.

$$N_d^i = \sum_{k=1}^{t} d_k^i \cdot N_k$$

$$N_a^j = \sum_{k=1}^{t} a_k^j \cdot N_k$$

N_d^i, N_a^j : total number of donor / acceptor sites of type i or j
d_k^i, a_k^j : number of donor / acceptor sites per molecule k

N_{ij} bonds can be distributed in Ω ways among N_i donor groups and N_j acceptor groups.

$$\Omega = \prod_{i=1}^{n} \frac{N_d^i!}{N_{i0}!} \prod_{j=1}^{m} \frac{N_a^j!}{N_{0j}!} \prod_{i=1}^{n} \prod_{j=1}^{m} \frac{\psi_{ij}^{N_{ij}}}{N_{ij}!} \qquad 5.4$$

ψ : probability factor of forming a hydrogen bond
$N_{i0} = N_d^i - \sum_{j=1}^{m} N_{ij}$: number of unbonded donor groups
$N_{0j} = N_a^j - \sum_{i=1}^{n} N_{ij}$: number of unbonded acceptor groups

Probability factor ψ is required, first, because two association groups have to be in close spatial proximity such that they can form a hydrogen bond. Therefore the probability factor is proportional to the density.

$$\psi_{ij} \propto {}^{n_{total}}\!/_{V} = \rho \qquad 5.5$$

An improvement of this model follows from the introduction of the donor - acceptor pair correlation function g_{ij} which is assumed to be the same as the segment - segment correlation function g_{kl} on which donor and acceptor groups reside[Gupta and Johnston (1994)].

$$\psi_{ij} \propto \rho \cdot g_{kl} \qquad 5.6$$

group i is part of component k
group j is part of component l

Second, it is necessary to take into account an entropic penalty (specific orientation of donor - acceptor, loss of rotational degrees of freedom) for hydrogen bonding.

$$\psi_{ij} = \exp\left(\frac{S_{ij}^{0}}{R}\right) \cdot \frac{\eta}{rN} \cdot g_{kl} \qquad 5.7$$

S_{ij}^{0} : association entropy

$rN = \sum_{k} r_k \cdot N_k$: total number of segments

The partition function $Q_{assoc.}$ can be written as a function of Ω and E_{ij}^{0}

$Q_{assoc.} = f(\Omega, E_{ij}^{0})$

E_{ij}^{0} : association energy

which leads to the following expression for the Helmholtz energy.

$$\frac{A_{assoc.}}{kT} = \sum_{i}\sum_{j} N_{ij}\left[1 + \frac{F_{ij}^{0}}{RT} + \ln\frac{N_{ij}\, rN}{N_{i0}N_{0j}} - \ln(g_{kl}\,\eta)\right] + \sum_{i} N_d^i \ln\frac{N_{i0}}{N_d^i} + \sum_{j} N_a^j \ln\frac{N_{0j}}{N_a^j} \qquad 5.8$$

$F_{ij}^{0} = E_{ij}^{0} - T \cdot S_{ij}^{0}$

The number of hydrogen bonds N_{ij} between donor group i and acceptor group j can be determined by finding the maximum term of the partition function. This is equivalent to the minimization of Helmholtz energy with respect to all kind of hydrogen bonds.

$$\left(\frac{\partial A_{assoc.}}{\partial N_{ij}}\right)_{T,V,\text{all } N_l, N_\alpha} = 0 \qquad 5.9$$

$$\frac{N_{ij}\, rN}{N_{i0}N_{0j}} = \eta \cdot g_{kl} \cdot \exp\left(\frac{-G_{ij}^{0}}{RT}\right) \qquad 5.10$$

$G_{ij}^{0} = E_{ij}^{0} - T \cdot S_{ij}^{0} + P \cdot V_{ij}^{0}$

V_{ij}^{0} : association volume

For pure fluids the influence of V_{ij}^{0} at temperatures lower than $0.9T_C$ is weak. Although it might become important in the critical and supercritical region, the pressure range considered in this work requires not the association volue parameter V_{ij}^{0} . For mathematicl simplicity it is therefore neglected ($V_{ij}^{0} = 0$). Equation 5.8 then becomes

$$\frac{A_{assoc.}}{kT} = \sum_i \sum_j N_{ij} + \sum_i N_d^i \ln \frac{N_{i0}}{N_d^i} + \sum_j N_a^j \ln \frac{N_{0j}}{N_a^j} \qquad 5.11$$

Expressions for chemical potential and pressure are given in appendix B.

$$\mu_k^{assoc.} = \left(\frac{\partial A_{assoc.}}{\partial N_k} \right)_{all\, N_i, V, T} \qquad 5.12$$

$$P = -\left(\frac{\partial A_{assoc}}{\partial V} \right)_{all\, N_i, T} \qquad 5.13$$

6. Results for pure fluids

Four classes of compounds have been examined.

- water
- 1-alkanols
- carboxylic acids
- glycols

The SAFT and Veytsman model require a definition of the number of donor and acceptor groups per molecule. The values used in this work are given below. It was found that the number of association sites per molecule has only a weak influence on the quality of pure-fluid data regression. However different parameter are obtained depending on the number of donor and acceptor sites.

	donor sites	acceptor sites
water	2	1
1-alkanols	1	1
carboxylic acids	1	1
glycols	2	2

To determine model parameters, experimental data for liquid density $\rho_{liq.}$ and vapor pressure $P_{sat.}$ in the temperature range of $T_{triple} < T < 0.9T_c$ have been used. Temperature-dependent data were obtained from the DIPPR data compilation [Daubert and Danner (1989)]. Non-linear least-squares regression is used to minimize objective function 6.1 for fifty equally spaced temperatures.

$$F = \sum_{i=1}^{50} \left(\frac{\rho_{liq.}^{calc.}(T_i) - \rho_{liq.}^{exp.}(T_i)}{\rho_{liq.}^{exp.}(T_i)} \right)^2 + \sum_{i=1}^{50} \left(\frac{P_{sat.}^{calc.}(T_i) - P_{sat.}^{exp.}(T_i)}{P_{sat.}^{exp.}(T_i)} \right)^2 \qquad 6.1$$

The use of five parameters cannot be justified by the number of experimental data. One way to overcome this problem is to fix one or more parameters à priori. Huang and Radosz (1990) used a fixed hard-sphere diameter σ. For larger molecules (like alkanols, carboxylic acids and amines), they have chosen the σ value of a CH_2 group which can be extrapolated from the homologous series of alkanes. For smaller molecules like water, ammonia and hydrogen sulfide, they used a slightly smaller value. On the other hand, Panayiotou and Sanchez (1991) proposed fixed values for the association energy and entropy. In this work we used the correlation of v.d.Waals surface areas $A^{surface}_{v.d.Waals}$ [Bondi (1968)] and the surface area $A^{surface}_{PHSC}$ calculated from PHSC parameters found for simple fluids [Song et al. (1994b)].

$$A^{surface}_{PHSC} = N_{AV} \cdot \pi \cdot r\sigma^2 \qquad 6.2$$

Equation 6.3 was used to correlated the surface areas of alkanes and to calculate the surface areas of all compounds discussed in this paper (s. figure 6.1) . The first part of equation 6.3 is used to force it through the origin and give a better fit in the region of small surface areas. Alkane parameters are given in appendix C.

$$A^{surface}_{PHSC} = \left[1 - \exp\left((c_1 \cdot A^{surface}_{v.d.Waals}\right)\right] \cdot \left[c_2 + c_3 \cdot A^{surface}_{v.d.Waals}\right] \qquad 6.3$$

$c_1 = -0.9549$

$c_2 = 0.18503$

$c_3 = 1.1251$

This method gives slightly better results especially for the density than that based on a correlation for volumes.

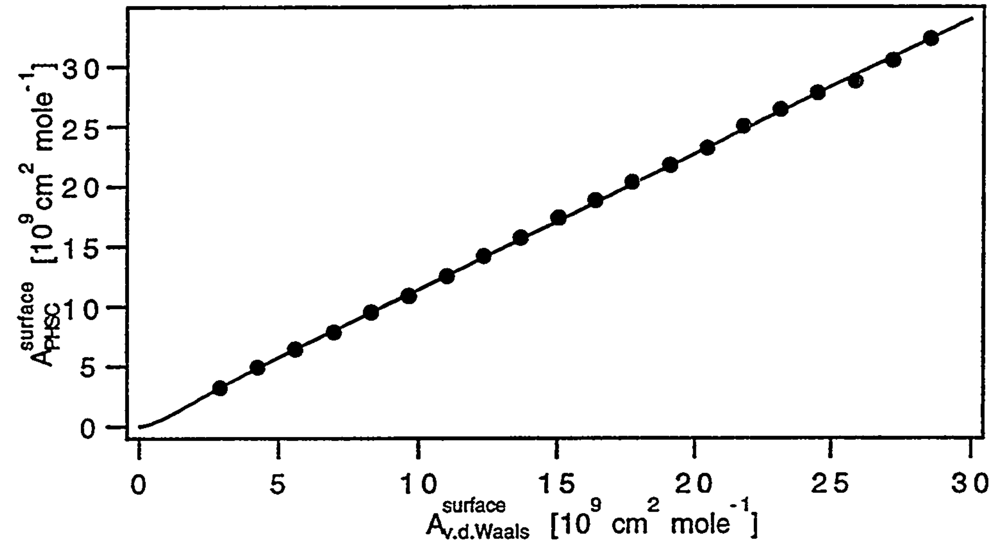


Figure 6.1 : Correlation of v.d.Waals and PHSC surface areas for alkanes

The ten Brinke / Karasz model gives no acceptable description of pure-fluid properties with physically meaningful parameters. Therefore, it is excluded from further considerations. Tables 6.1 and 6.2 give results of the four-parameter fit (σ, ε, E^0_{ij} and κ_{ij} or S^0_{ij} in case of the Veytsman model, r is given by equation 6.2 and 6.3) for the combination of PHSC with SAFT, respectively with the Veytsman association model. Although the derivation of these two models is very different, the final results can be expressed in very similiar equations as shown by Economou and Donohue (1991) Therefore the strong correlation between the parameter sets found for SAFT and the Veytsman extension of the PHSC theory is not a surprise (s. figures 6.2 - 6.6). The adjusted values for r, σ, ε and E^0_{ij} are nearly identica. The correlation function for κ_{ij} and S^0_{ij} is shown in figure 6.6. Both models describe pure-fluid properties with similar deviations.

	r	σ[Å]	ε/k [K]	$E^0_{A_iB_j}$/R [K]	$\kappa_{A_iB_j}$	% rms ρ	% rms P
Water	1.2329	3.1461	328.3	2611.4	2.254E-02	1.24	5.34
Methanol	1.3063	4.0606	401.8	2026.3	5.404E-03	3.64	3.80
Ethanol	1.8202	4.0613	286.7	2478.3	8.800E-03	1.94	3.28
1- Propanol	2.2558	4.1167	301.8	2433.3	3.419E-03	2.31	6.42
1-Butanol	2.7036	4.1392	278.2	2570.0	4.793E-03	3.00	4.82
1-Pentanol	3.2733	4.0757	281.3	2647.6	1.526E-03	4.86	8.60
1-Hexanol	3.7151	4.0986	250.9	2495.4	1.554E-02	4.95	2.83
1-Heptanol	4.1412	4.1242	265.3	2902.2	1.993E-03	5.72	4.17
1-Octanol	4.6480	4.1088	255.7	2715.9	5.635E-03	5.86	2.67
1-Nonanol	5.4001	4.0022	248.9	2829.0	3.953E-03	7.69	4.48
1-Decanol	5.8046	4.0354	243.6	2685.2	1.076E-02	6.81	3.49
1-Undecanol	6.5752	3.9493	242.4	2911.5	2.571E-03	7.54	3.29
1-Dodecanol	6.8962	4.0044	241.0	2711.5	9.922E-03	7.04	2.66
1-Tridecanol	7.8302	3.8920	232.4	2602.4	1.048E-02	7.95	1.80
1-Tetradecanol	8.2640	3.9146	231.4	2857.7	7.851E-03	7.96	2.31
1-Pentadecanol	9.2229	3.8212	218.8	2445.0	6.405E-02	8.75	0.98
1-Hexadecanol	9.7893	3.8179	224.5	2888.8	8.247E-03	8.46	3.22
Formic acid	2.2053	3.2394	225.8	1911.6	5.499E-01	1.61	4.91
Acetic acid	2.1294	3.8496	268.8	2026.3	1.482E-01	0.63	2.29
Propionic acid	2.5212	3.9699	256.3	2545.8	5.785E-02	1.08	1.76
Butanoic acid	2.8574	4.0907	262.1	2732.8	3.607E-02	1.75	1.57
Pentanoic acid	3.1875	4.1863	273.4	2737.1	2.902E-02	1.97	1.79
Hexanoic acid	3.5892	4.2192	279.5	3113.9	9.689E-03	3.09	2.40
1,2-Ethanediol	2.6800	3.5743	203.9	2518.9	4.220E-02	2.07	6.64
1,2-Propanediol	2.9031	3.8178	279.8	1997.6	2.144E-02	5.40	13.88
1,3-Propanediol	3.9082	3.2928	125.7	2877.5	9.088E-02	3.58	9.63
1,2-Butanediol	3.8184	3.6323	154.1	2895.9	3.226E-02	3.55	4.02
1,3-Butanediol	3.0489	4.0649	333.6	2117.3	4.734E-03	4.54	16.16
1,4-Butanediol	4.3123	3.4200	140.5	3084.7	5.714E-02	2.93	7.19
2,3-Butanediol	4.1732	3.4766	143.5	2603.0	5.862E-02	2.90	5.17
1,5-Pentanediol	4.7534	3.5075	147.1	3104.4	5.735E-02	3.47	5.82
2,2-Dimethyl-1,3-Propanediol	3.1178	4.3726	212.7	3106.3	8.678E-03	1.40	0.98
1,6-Hexanediol	4.8090	3.7190	176.5	3158.3	2.811E-02	1.79	2.70
2-Methyl-2,4-Pentanediol	4.3964	3.9208	208.3	2791.8	1.007E-02	5.01	5.51

Table 6.1 Parameter for PHSC theory combined with the SAFT association model

	r	σ[Å]	ε/k [K]	$E^0_{A_iB_j}/R$ [K]	$S^0_{A_iB_j}/R$	% rms ρ	% rms P
Water	1.2300	3.1499	329.7	-2540.7	-2.5133	1.27	5.16
Methanol	1.3073	4.0591	404.9	-1945.4	-4.0325	3.60	4.05
Ethanol	1.8245	4.0565	286.1	-2422.7	-3.4386	1.94	3.52
1- Propanol	2.2879	4.0878	299.9	-2357.9	-4.3679	2.46	6.67
1-Butanol	2.7102	4.1342	277.5	-2513.7	-4.0288	3.01	4.89
1-Pentanol	3.2386	4.0974	283.2	-2608.5	-5.2840	4.68	8.72
1-Hexanol	3.7164	4.0979	250.5	-2448.3	-2.8664	4.94	2.81
1-Heptanol	4.1411	4.1244	265.2	-2847.0	-4.9175	5.72	4.16
1-Octanol	4.6472	4.1091	255.7	-2664.1	-3.8820	5.86	2.65
1-Nonanol	5.4021	4.0015	248.9	-2776.9	-4.2351	7.69	4.46
1-Decanol	5.8049	4.0353	243.5	-2635.6	-3.2327	6.80	3.48
1-Undecanol	6.5726	3.9501	242.4	-2860.2	-4.6600	7.54	3.29
1-Dodecanol	6.9012	4.0029	241.0	-2660.3	-3.3138	7.04	2.65
1-Tridecanol	7.8350	3.8908	232.3	-2552.1	-3.2539	7.95	1.81
1-Tetradecanol	8.2618	3.9151	231.6	-2814.9	-3.5773	7.97	2.31
1-Pentadecanol	9.2290	3.8199	218.8	-2398.9	-1.4545	8.74	0.98
1-Hexadecanol	9.7598	3.8237	225.1	-2888.1	-3.6761	8.45	3.22
Formic acid	2.2858	3.1818	217.0	-1914.4	0.7491	2.03	4.88
Acetic acid	2.1730	3.8108	261.2	-2025.8	-0.5938	0.88	2.37
Propionic acid	2.5405	3.9548	253.5	-2514.6	-1.5409	1.20	1.77
Butanoic acid	2.8698	4.0818	260.4	-2692.7	-2.0173	1.81	1.55
Pentanoic acid	3.1946	4.1816	272.2	-2693.1	-2.2378	2.00	1.77
Hexanoic acid	3.5905	4.2184	279.3	-3058.6	-3.3383	3.09	2.37
1,2-Ethanediol	2.6648	3.5845	205.8	-2466.9	-1.8776	2.02	6.64
1,2-Propanediol	2.9572	3.7827	246.5	-2171.7	-2.3844	4.65	14.59
1,3-Propanediol	3.9525	3.2743	125.0	-2825.3	-0.9856	3.61	8.83
1,2-Butanediol	3.7825	3.6496	156.6	-2837.4	-2.1149	3.38	3.75
1,3-Butanediol	2.9704	4.1183	334.7	-2100.4	-4.0801	3.99	15.93
1,4-Butanediol	4.3308	3.4127	140.3	-3027.5	-1.4699	2.95	6.64
2,3-Butanediol	4.1777	3.4747	143.5	-2553.9	-1.4762	2.92	4.84
1,5-Pentanediol	4.7552	3.5069	147.8	-3046.0	-1.4925	3.37	5.27
2,2-Dimethyl-1,3-Propanediol	3.1078	4.3796	213.7	-3049.8	-3.4387	1.40	0.95
1,6-Hexanediol	4.7565	3.7395	178.7	-3096.0	-2.2598	1.70	2.62
2-Methyl-2,4-Pentanediol	3.9441	4.1395	225.0	-2762.4	-3.6668	2.88	6.07

Table 6.2 Parameters for the PHSC theory combined with the Veytsman association model

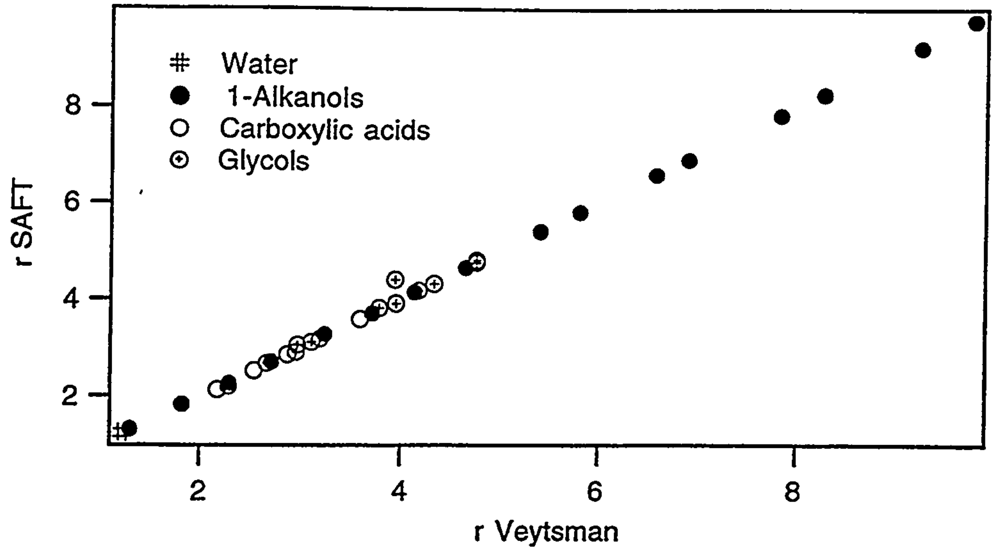


Figure 6.2 Correlation of r parameters of SAFT and Veytsman extension of PHSC theory

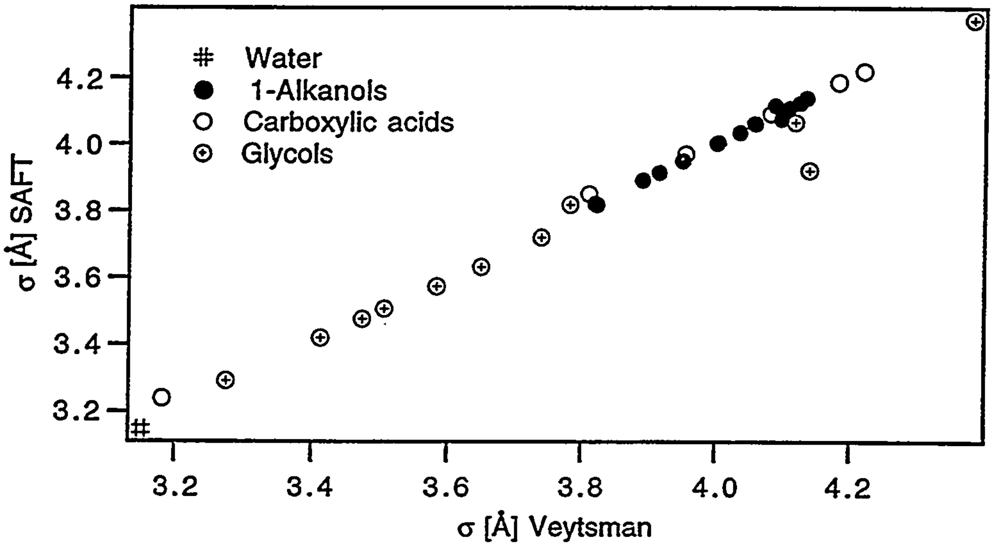


Figure 6.3 Correlation of σ parameters of SAFT and Veytsman extension of PHSC theory

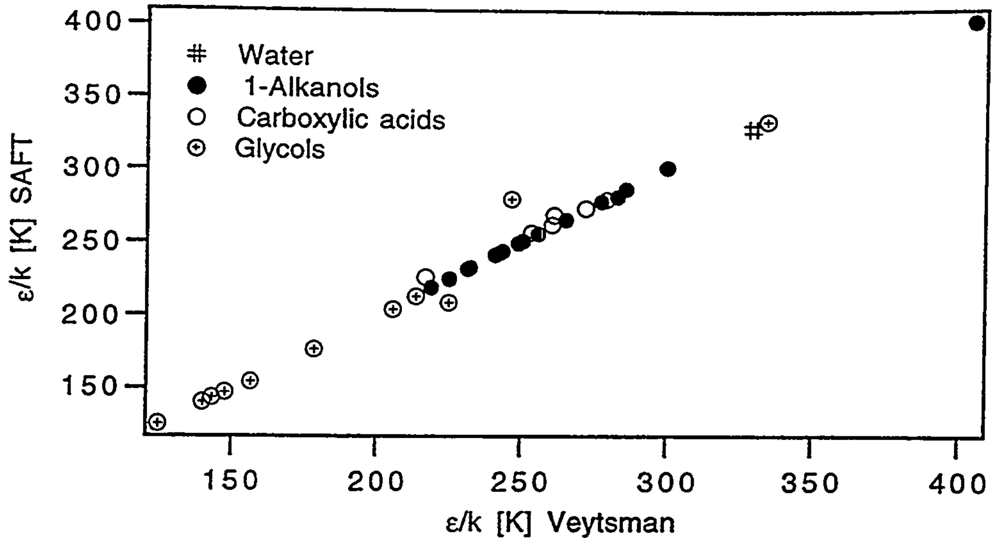


Figure 6.4 Correlation of ε parameters of SAFT and Veytsman extension of PHSC theory

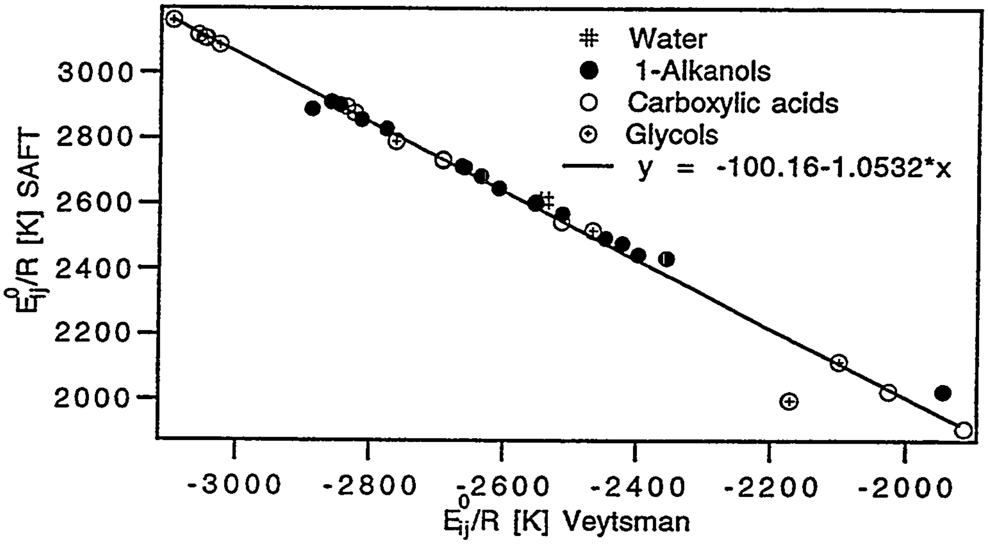


Figure 6.5 Correlation of association energy E_{ij}^0 parameters of SAFT and Veytsman extension of PHSC theory

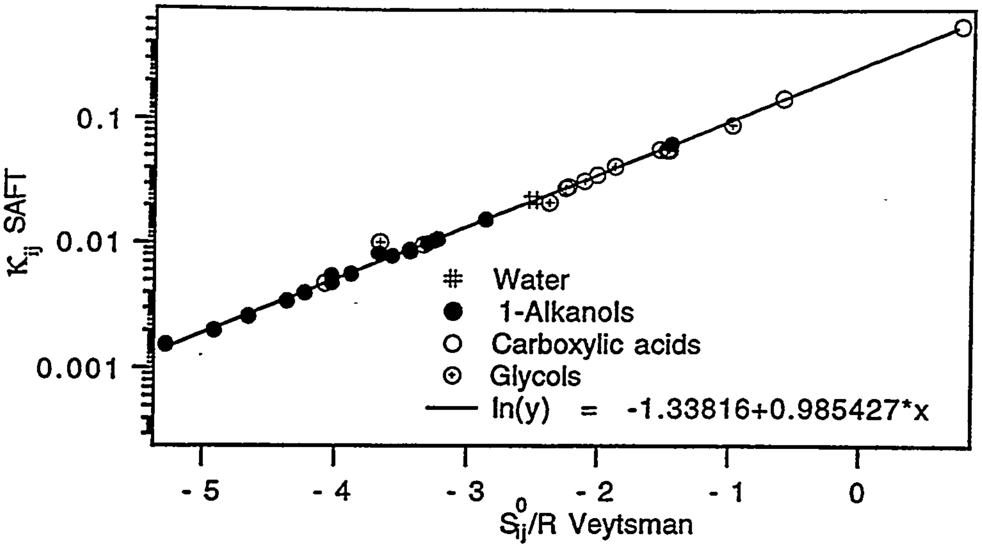


Figure 6.6 Correlation of association volume κ_{ij} and association entropy S^0_{ij} of SAFT and Veytsman extension of PHSC theory

7. Results for mixtures

SAFT and the Veytsman extension of the PHSC theory show similar results for the regression of pure-fluid data. The parameter sets are strongly correlated for the examined compounds. To determine the differences between the two association models, we have studied some simple binary mixtures. All systems examined so far have only one kind of donor site and one kind of acceptor site which means that only one kind of hydrogen bonding occurs either between molecules of the same species or between molecules of different species. To study the general influence of the different model parameters we have carried out some calculations for model systems with hypothetical components. The parameters were chosen arbitarily but in a physical meaningful range. When not mentioned otherwise, the following parameters were used for the calculations :

T : 300 K, P : 1 bar

r_1	: 2	r_2	: 2
σ_1	: 3.5 Å	σ_2	: 3.5 Å
ε_1/k	: 300 K	ε_2/k	: 300 K

E^0_{ij}/R : 2000 K	κ_{ij} : 0.04568	for SAFT association part
E^0_{ij}/R : -2000 K	S^0_{ij}/R : -2.0	for Veytsman association part

Model calculations were first carried out with hydrogen bonding only between molecules of component 1. Component 1 has one donor site and 1 acceptor site.Hydrogen bonding can only occur between donor sites and acceptor sites, not between two sites of the same kind. This means in terms of the SAFT model one association site A and one association site B with interactions only between A and B, not between sites of the same type. Component 2 is inert to hydrogen bonding and interacts only in a non-specific way with component 1. This picture is usually used to describe mixtures of alkanols (component 1) in inert solvents like alkanes (component 2). Figure 7.1 shows the concentration dependence ($\phi_1 = x_1 r_1 / \sum_k x_k r_k$, segment fraction of component 1) of the chemical potential due to hydrogen bonding $\mu_k^{assoc.}$ for different values of r_2. Figure 7.2 presents results for different ratios of σ_2/σ_1 (σ_1 = const.), figure 7.3 gives the temperature dependence of the chemical potentials for infinite dilution of 2 in 1 ($\phi_1 = 1$).

Both models give the same results for the chemical potential and its concentration and temperature dependence as long as the hard-sphere diameters of both components are equal ($\sigma_1 = \sigma_2$). With increasing difference of σ_1 and σ_2 the differences in the chemical potentials increase (s. Figure 7.4).

This result is independent of the assumption that hydrogen bonding occurs only between molecules of component 1 with one donor and one acceptor site. It was also found for systems with hydrogen bonding between component 1 and component 2 (component 1 with one donor site, component 2 with one acceptor site; chloroform - ether like association; s. figures 7.5 and 7.6) and for water - inert solvent like systems (component 1 has two donor sites and one acceptor site). Fort chloroform-ether-like association, the association strength $\Delta^{A_1B_2}$ for the SAFT model is defined in terms of σ_1 only (not in terms of σ_{12}) to keep $\kappa_{A_iB_j}$ constant for different values of σ_2.

$$\Delta^{A_1B_2} = \sigma_{11} \cdot \kappa_{A_1B_2} \cdot g(d_{12}) \cdot \left[\exp\left(\frac{E^0_{A_1B_2}}{kT} \right) - 1 \right]$$

Both models give not only the same association part of the chemical potential as function of temperature and concentration but also the same fraction of unbonded association sites as long as σ_1 equals σ_2.

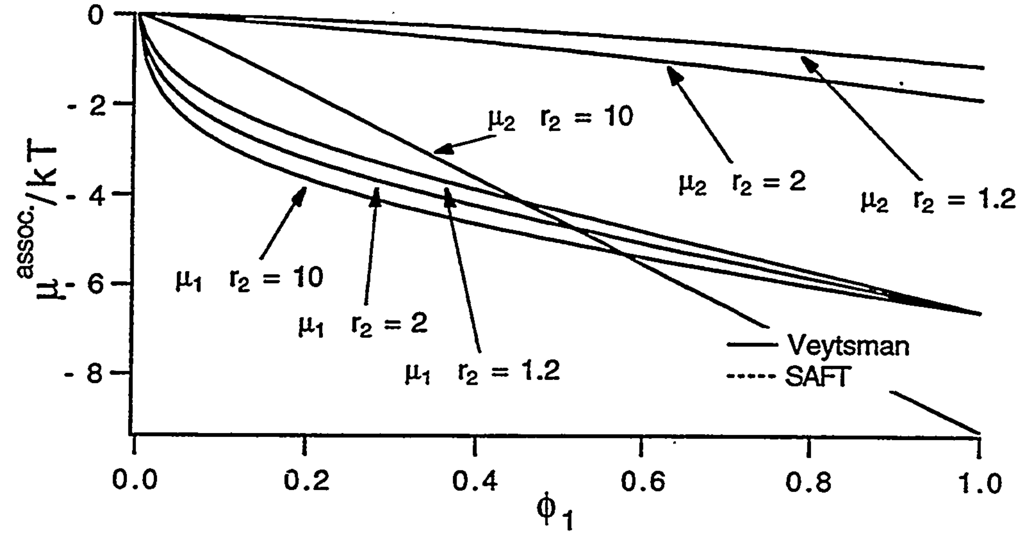


Figure 7.1 Concentration dependence of the chemical potential due to hydrogen bonding for different chain lengths of component 2 (hydrogen bonding only between molecules of component 1).

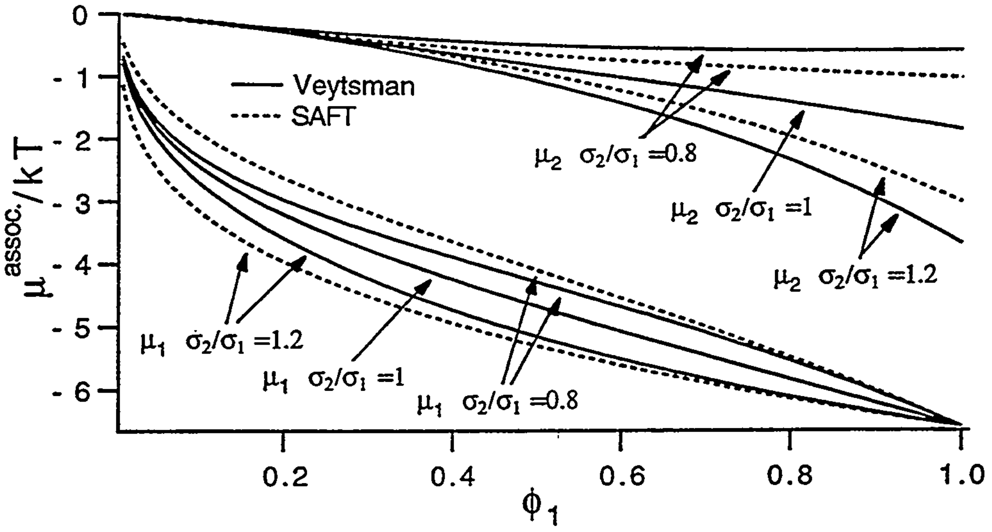


Figure 7.2 Concentration dependence of the chemical potential due to hydrogen bonding for different ratios of σ_2/σ_1 (σ_1 = const.) (hydrogen bonding only between molecules of component 1).

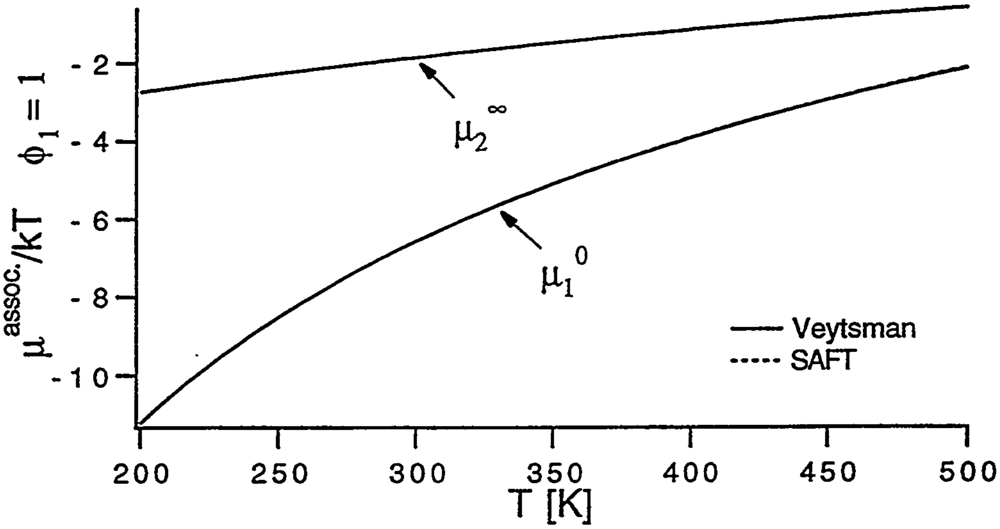


Figure 7.3 Temperature dependence of the chemical potential due to hydrogen bonding for infinite dilution of component 2 in 1 (ϕ_1=1.0) (hydrogen bonding only between molecules of component 1).

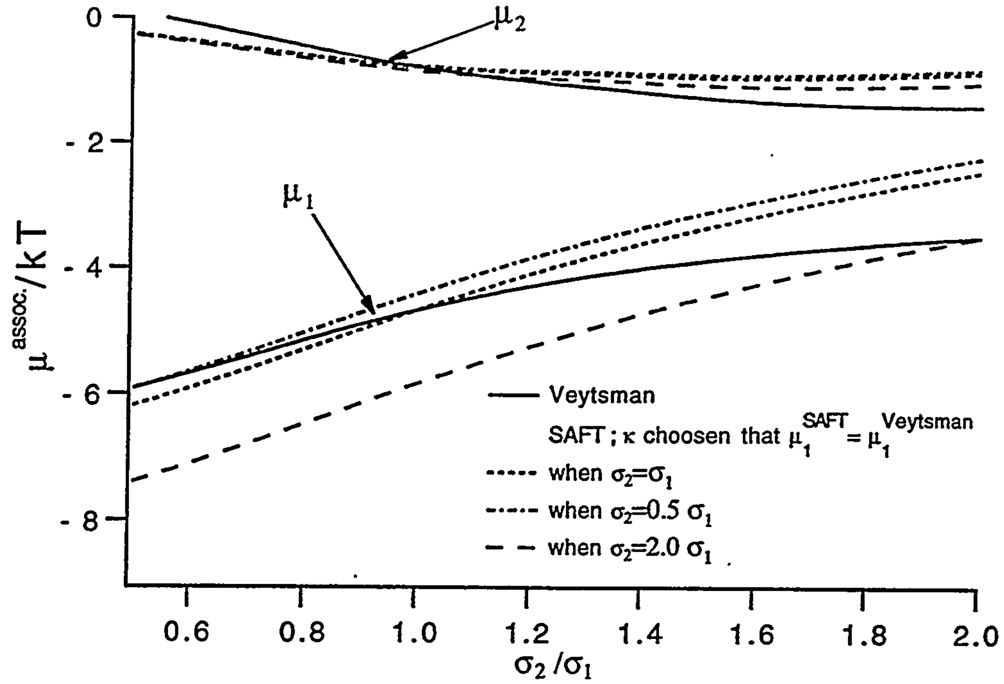


Figure 7.4 Association part of the chemical potential as function of different ratios of σ_2/σ_1 (σ_1 = const.) (hydrogen bonding only between molecules of component 1).

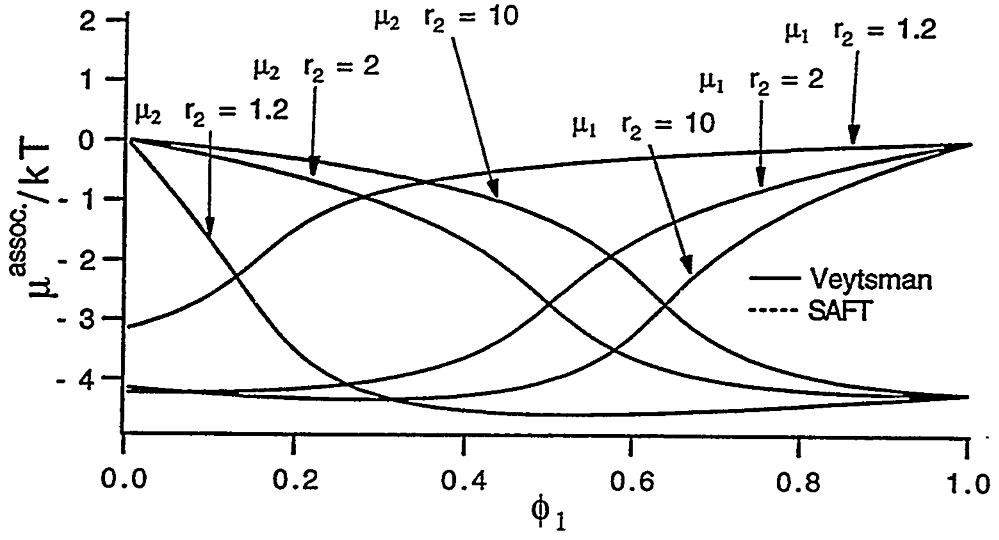


Figure 7.5 Concentration dependence of the chemical potential due to hydrogen bonding for different chain lengths of component 2 (hydrogen bonding only between molecules of component 1 and component 2).

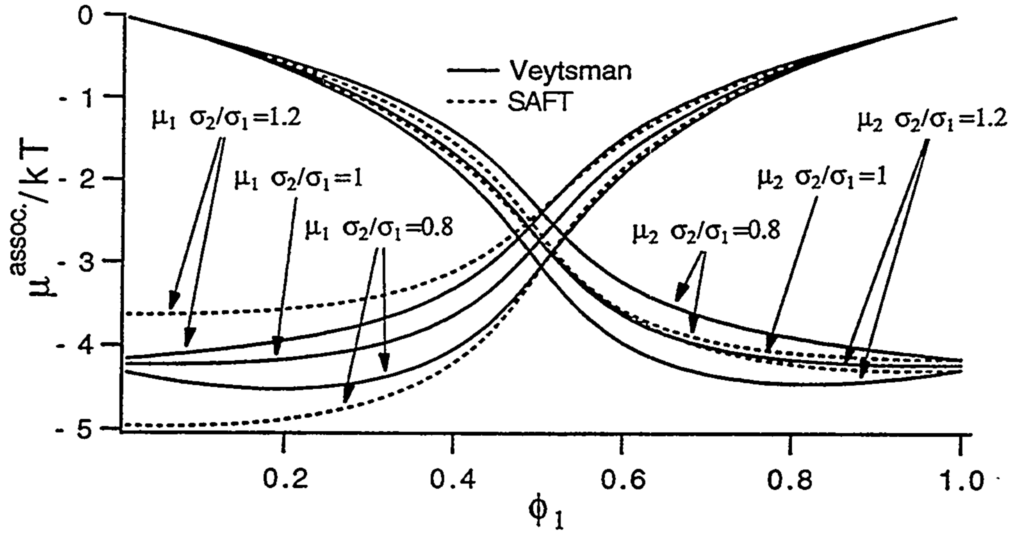


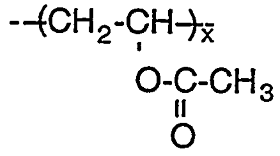
Figure 7.6 Concentration dependence of the chemical potential due to hydrogen bonding for different ratios of σ_2/σ_1 (σ_1 = const.) (hydrogen bonding only between molecules of component 1 and component 2).

To compare both association models with regard to application to real systems, we have chosen VLE and LLE data for some representative systems.

7.1 VLE data

For systems like alkanols in alkanes differences in the prediction of VLE data are not significant. VLE data are not sensitive to small differences in the association part of the chemical potential. In the vapor phase, the contribution of the chemical potential due to hydrogen bonding is nearly neglectible because of the low density; in the liquid phase, the differences between the two models have to be seen with regard to the sum of all five contributions to the total chemical potential. Therefore, when comparing models, the relative deviation in the sum of all contributions to the chemical potential is very small.

Figures 7.1.1 - 7.1.3 show results for two systems containing polymers. Hydrogen bonding occurs only between the solvent chloroform and the polymer molecules [poly(vinyl acetate) PVA or poly(ethylene oxide) PEO]. Compared to the results of the PHSC theory, the additional interaction between solvent and polymer decreases the vapor pressure, as expected.Association parameter E^0_{ij} and κ_{ij} or S^0_{ij} are adjusted to the experimental data. For poly(vinyl acetate), the number of acceptor sites per repeat unit is not obvious.



$$-(CH_2-\underset{\underset{\underset{O}{\|}}{O-C-CH_3}}{CH})_x-$$

PVA

$(CH_2-CH_2-O)_x$

PEO

We have tested one and two acceptor sites. The quality of the fit is hardly influenced by the number of association sites although the parameters are. This is in agreement with the results for pure fluids. Association parameters for poly(ethylene oxide) are obtained only by fitting the experimental data containing the high-molecular-weight polymer (s. figure 7.1.2). The vapor pressure of the system containing low-molecular-weight poly(ethylene oxide) is predicted by using these parameters. Pure polymer data are obtained from PVT data [Lambert (1994)].

	PVA	PEO
r/M	$5.165929 \cdot 10^{-2}$	$4.77775 \cdot 10^{-2}$
σ [Å]	3.3465	3.5321
ε/k [K]	292.6	316.6
MW per repeat unit [g/mole]	86.09	44.05

Table 7.1.1 PHSC parameters for PVA and PEO

	Chloroform
r	2.887
σ [Å]	3.7261
ε/k [K]	268.1

Table 7.1.2 PHSC parameters for Chloroform

	E^0_{ij}/R [K]	κ^0_{ij}
PVA 1 acceptor / repeat unit	2719.6	$3.2386 \cdot 10^{-4}$
PVA 2 acceptor / repeat unit	2088.5	$9.6987 \cdot 10^{-4}$
PEO1 all data points included in parameter fit	1503.8	$1.0474 \cdot 10^{-2}$
PEO2 some data points excluded of parameter fit	1441.9	$1.3865 \cdot 10^{-2}$

Table 7.1.3 Association parameters for Chloroform - PVA / PEO (SAFT model)

	E^0_{ij}/R [K]	S^0_{ij}/R
PVA 1 acceptor / repeat unit	-2321.5	-5.5909
PVA 2 acceptor / repeat unit	-1704.7	-4.6367
PEO1 all data points included in parameter fit	-1349.7	-3.0132
PEO2 some data points excluded of parameter fit	-1303.2	-2.7758

Table 7.1.4 Association parameters for Chloroform - PVA / PEO (Veytsman model)

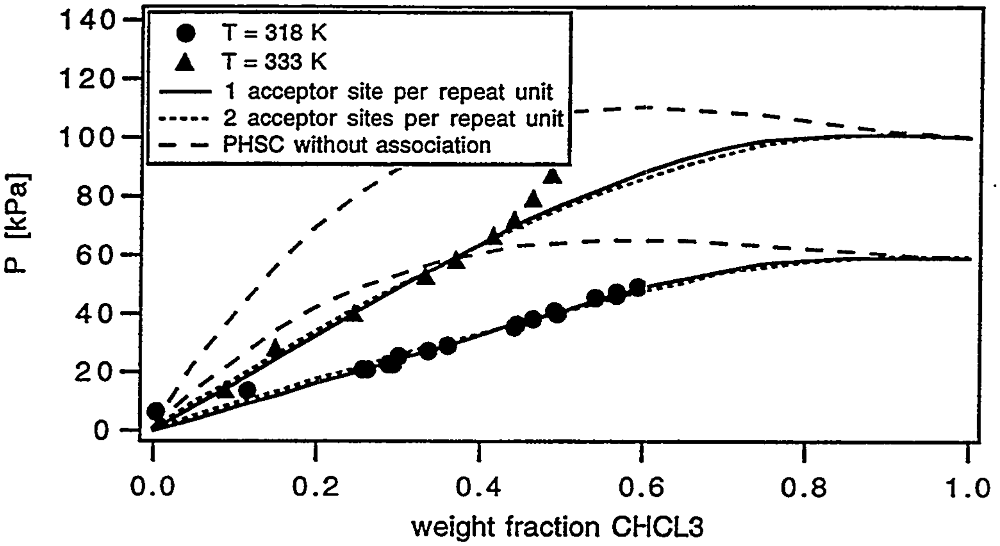


Figure 7.1.1 Vapor pressure of chloroform - poly(vinyl acetate).
Experimental data by Gupta (1994)

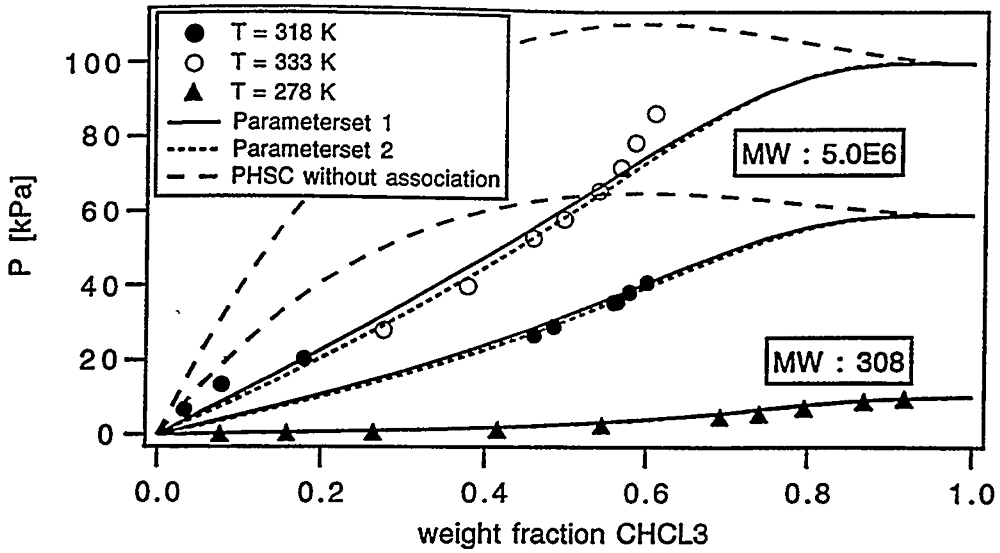


Figure 7.1.2 Vapor pressure of chloroform - poly(ethylene oxide). Experimental data by Gupta (1994) and Malcolm et al. (1969).

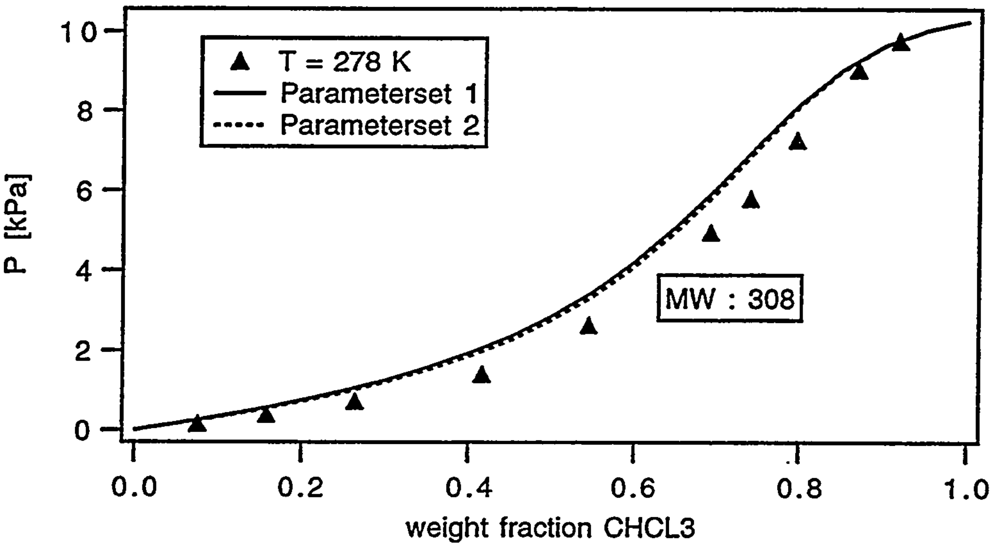


Figure 7.1.3 Prediction of vapor pressure for chloroform - poly(ethylene oxide). Experimental data by Malcolm et al. (1969).

7.2 LLE-data

Liquid - liquid equilibrium is much more sensitive than VLE to small changes in the chemical potential. The properties of both fluid phases are much more similar for VLE which causes a very delicate balance between the two liquid phases. Representation of LLE data is therefore much more sensitive to model parameters and provides a crucial test for model equations.

The first system examined is methanol in different alkanes (s. figure 7.2.1, parameters for pure alkanes s. appendix C). Although the parameters for the pure alkanes are not smoothed, the Veytsman extension represents nicely the increasing UCST (upper critical solution temperature) with increasing molecular weight of the alkane. The only exception is pentane as solvent. The SAFT extension cannot predict this trend. Results are not a monotonic function of the molecular-weight of the alkanes but the general tendency predicted by the SAFT association model is wrong.

Both extensions of the PHSC are not able to predict the critical temperature and the critical composition. These properties are very sensitive to model parameters which are not unique. A slight change in the objective function (s. chapter 6) yields different pure-component parameters and influences the calculated values for critical temperature and critical composition. In addition the calculated binodal curves are too narrow in the critical region because non-random mixing and fluctuation effects have been neglected.

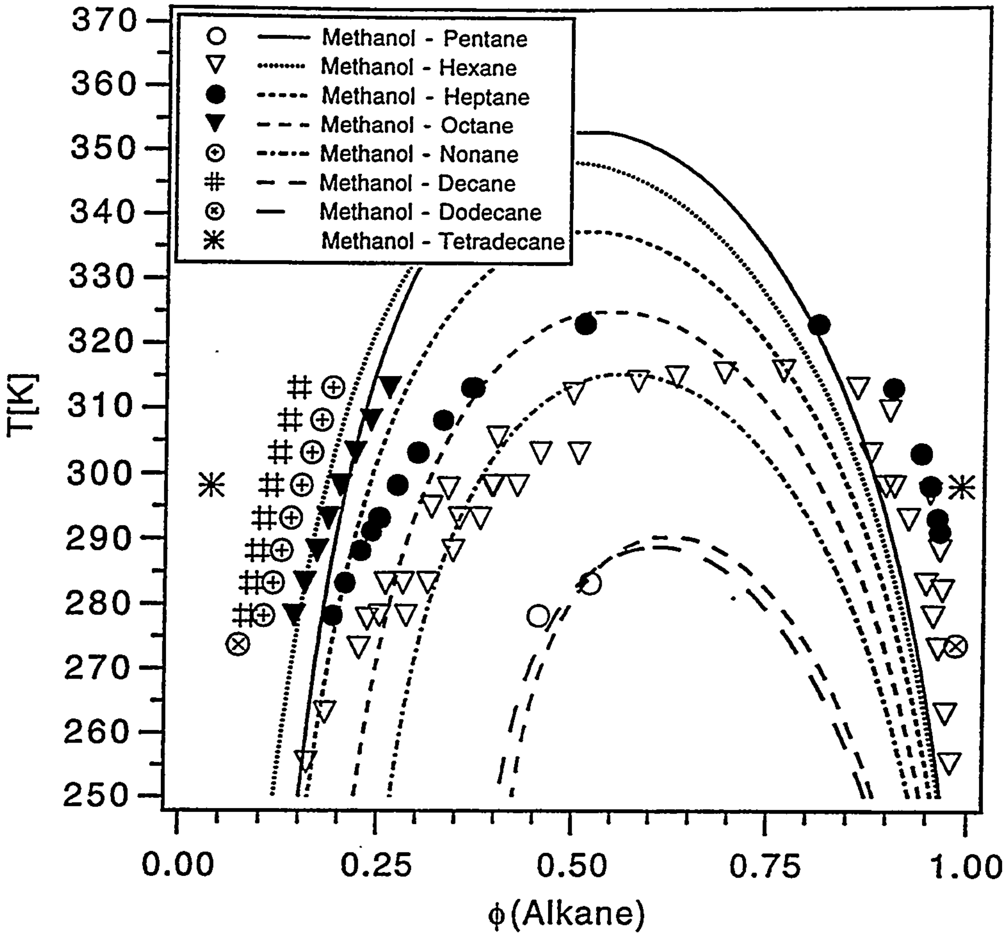


Figure 7.2.1 Prediction of LLE for methanol in different alkanols by PHSC/SAFT model. T_c predicted for methanol - tetradecane is 170 K. Experimental data taken from Sørensen and Arlt, Liquid-Liquid Equilibrium Data Collection 1979.

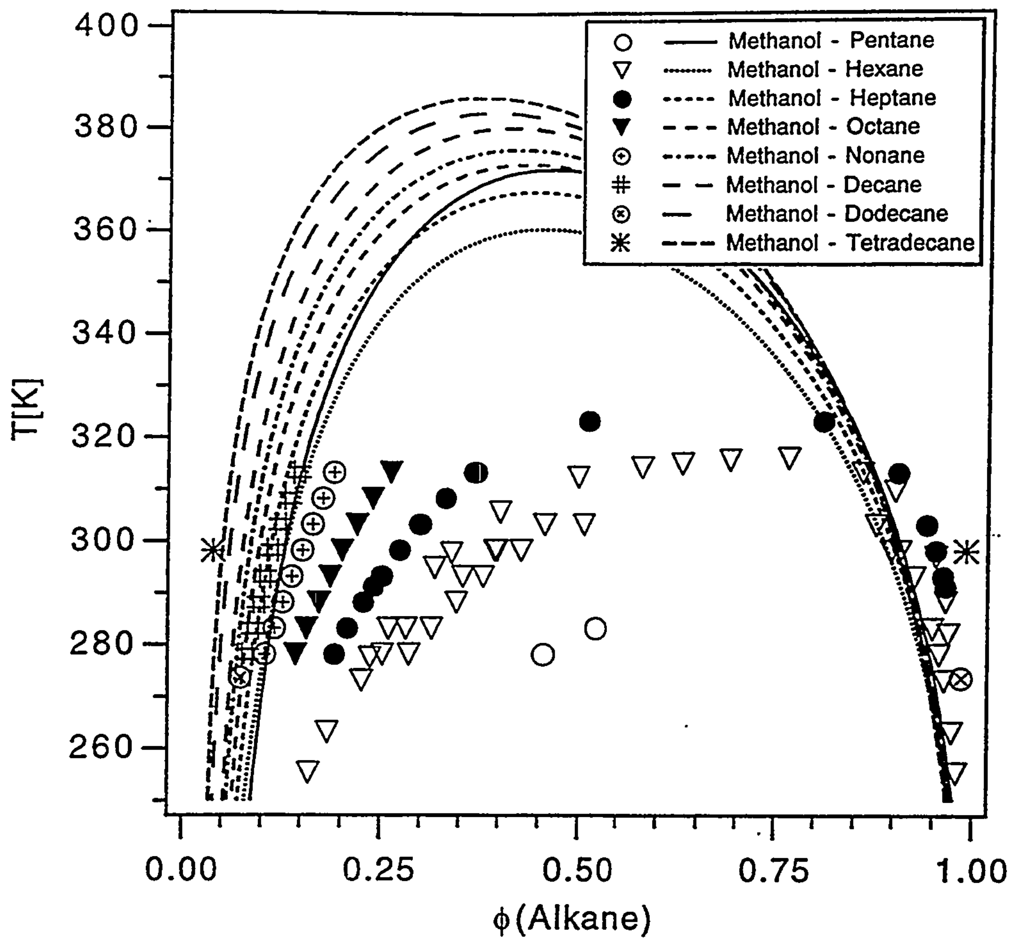


Figure 7.2.1 Prediction of LLE for methanol in different alkanols by PHSC/Veytsman model. Experimental data taken from Sørensen and Arlt, Liquid-Liquid Equilibrium Data Collection 1979.

For mixtures of water in alkanes, both models succeed in predicting the increase of the UCST with increasing chain length of the alkane. The results of both models are nearly the same in the alkane-rich phase but differ in the water-rich region where SAFT gives slightly better values for the concentration of the alkane. This is in agreement with figure 7.2. The chemical potential of the associating component is equal for both models for the pure fluid and at infinite dilution. The chemical potential of the non-associating component is zero for both models in case of the pure fluid but the results differ significantly at infinite dilution, when the hard-sphere diameters of both components are not equal.

To extend the examination of LLE to systems containing polymers, we have chosen mixtures of polyethylene of different molecular weight in different alkanols.

Parameters for pure polyethylene obtained from PVT data cannot be used to describe the experimental results. Both models were not able to predict a UCST for any example using these polyethylene parameters. Therefore, polyethylene parameters are obtained by extrapolation of alkane parameters to infinite molecular weight..

	r/M [mole/g]	σ [Å]	ε/k [K]
HDPE (only PVT data)	$4.93801 \cdot 10^{-2}$	3.8249	324.1
LDPE1 (only PVT data)	$4.51781 \cdot 10^{-2}$	3.9620	337.7
LDPE2 (only PVT data)	$3.36823 \cdot 10^{-2}$	3.5881	362.0
LLDPE (only PVT data)	$5.85352 \cdot 10^{-2}$	3.6030	306.0
extrapolated from alkanes	$4.51100 \cdot 10^{-2}$	3.7000	214.0

Table 7.2.1 PHSC parameters for PE

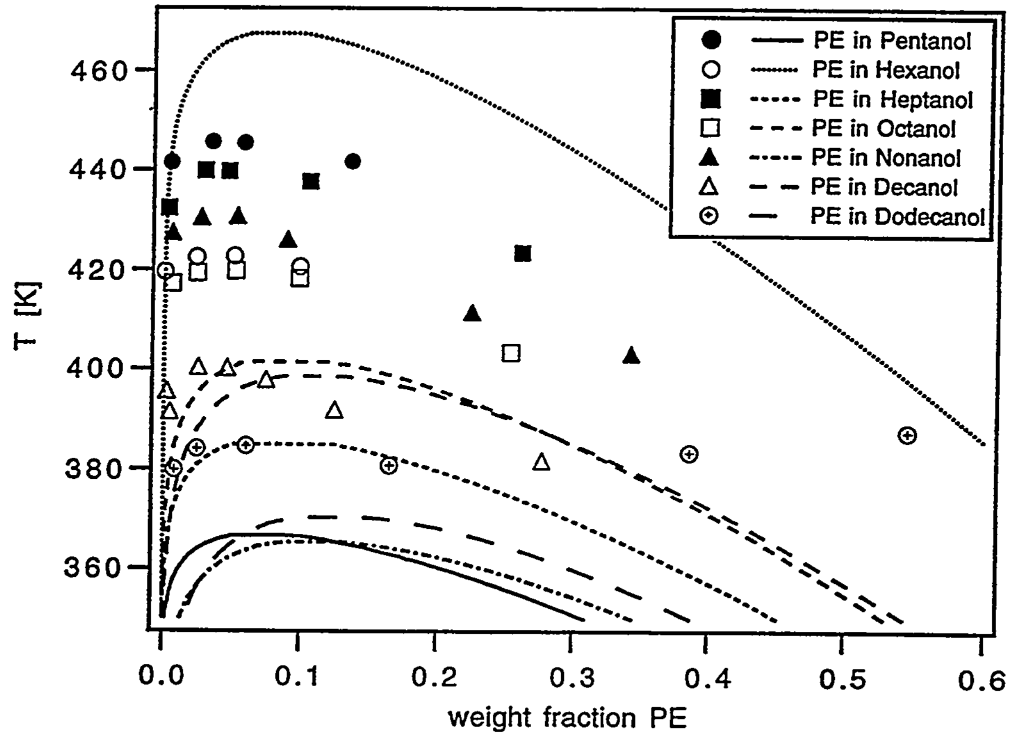


Figure 7.2.3 Prediction of LLE for Polyethylene (MW : 20000) in different alkanols with PHSC/Veytsman model. Experimental data by Nakajima et al. (1966)

Figure 7.2.3 shows the influence of different solvents. Although theoretical and experimental data are not monotonic decreasing with increasing molecular-weight of the alkanol, the general trend of decreasing UCST with increasing chain length of the alkanol is predicted by the Veytsman extension. The SAFT extension does not predict a UCST which is not surprising, considering the results of the methanol - alkane systems.

The Veytsman association part enables the PHSC theory also to predict the right molecular-weight dependence of the UCST and LCST (lower critical solution temperature) for different chain lengths of polyethylene in 1-octanol (figures 7.2.4 and 7.2.5). The SAFT extension failed to give the UCST but the results for the LCST are very similar to those of the Veytsman extension. This was expected because at temperatures higher than 600 K the contribution of the association to any thermodynamic property is usually small.

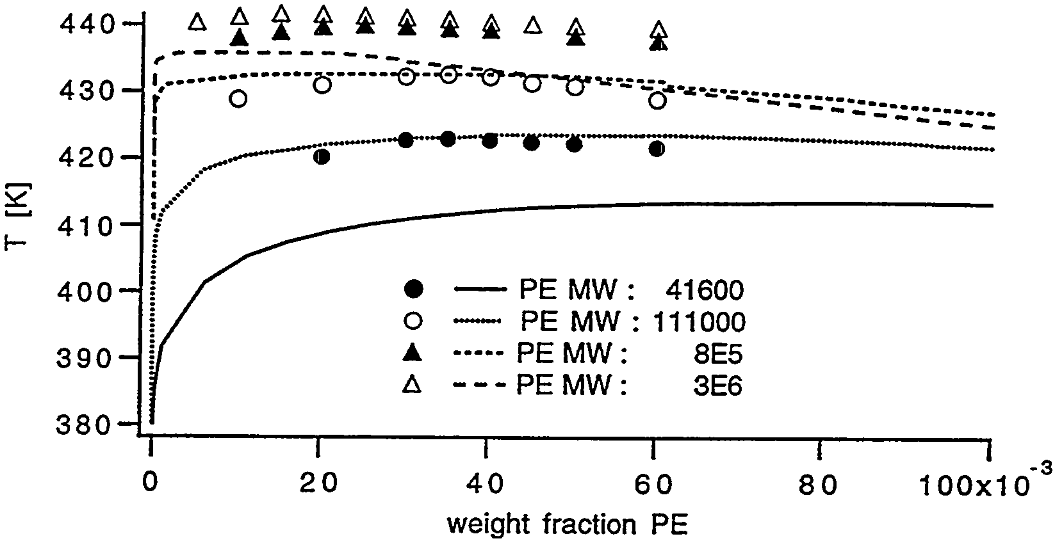


Figure 7.2.4 UCST for PE of different molecular weight in 1-octanol. Experimental data by Muraoka et al. (1983).

The critical composition can be matched by adjusting the r/M parameter of the polymer. The critical temperature can be adjusted by using the binary parameter k_{ij}. However, for polymers of different molecular-weight these two parameters have to be molecular-weight dependent (s. figure 7.2.6).

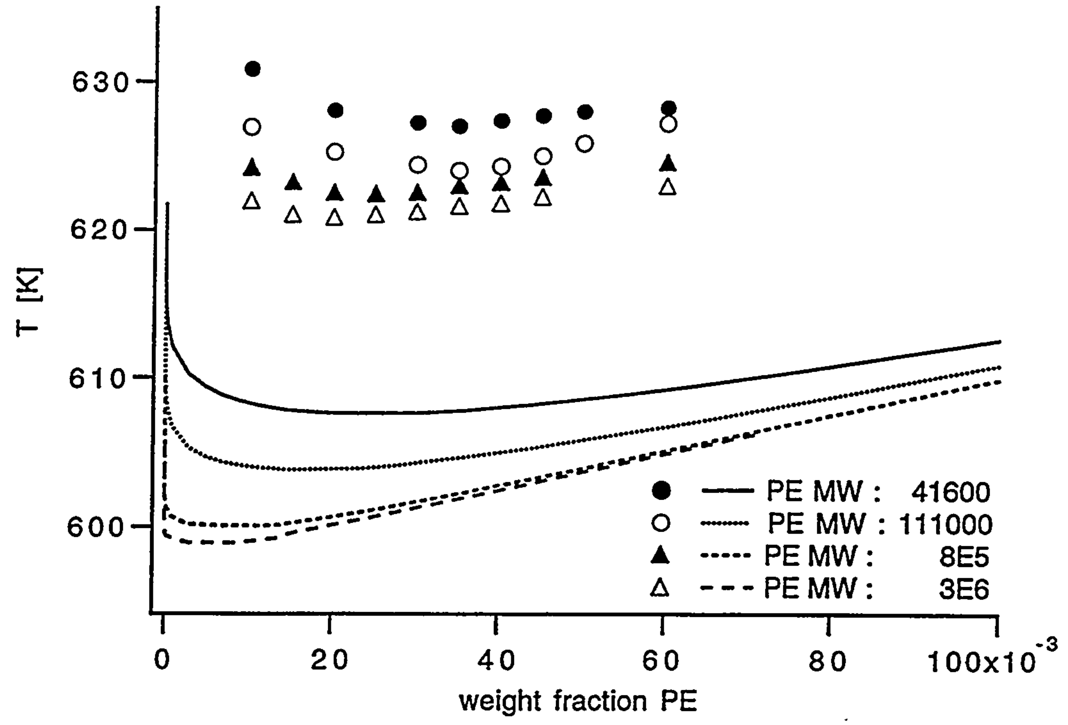


Figure 7.2.5 LCST for PE of different molecular weight in 1-octanol. Experimental data by Muraoka et al.(1983).

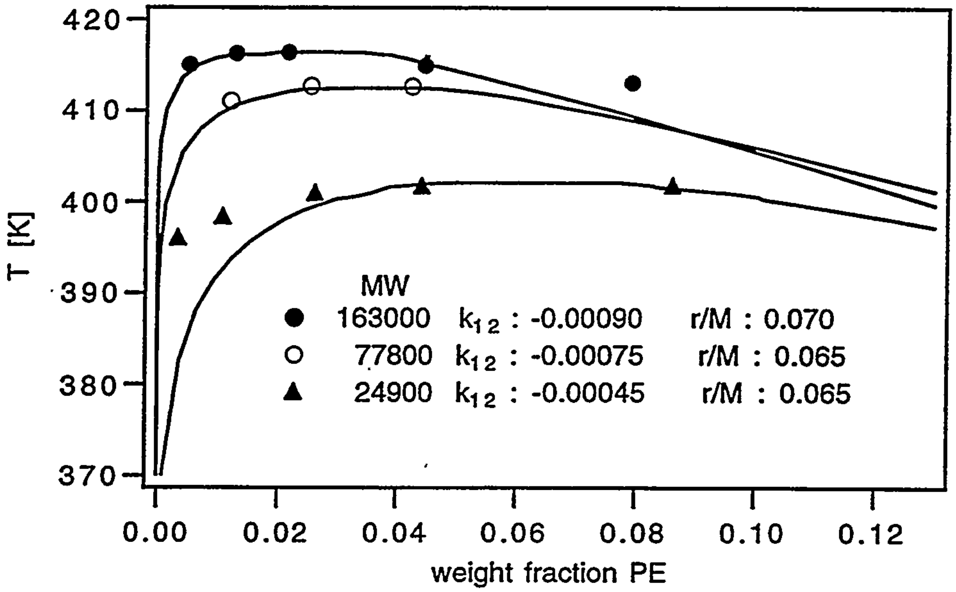


Figure 7.2.6 Description of LLE for PE in 1-decanol. r/M is adjusted to match the critical composition, k_{12} is adjusted to match the critical temperature.

Extension of the PHSC theory with both association models enables the theory to describe closed loop phase diagrams upon assuming hydrogen bonding between component 1 and component 2. In principle, all observed types of binary phase diagrams can be described although quantitative agreement is often poor.

8. Conclusions

The ten Brinke / Karasz model is easy to use but the parameters obtained from data regression of pure-fluid data have no physical significance. No prediction of properties of mixtures is possible . Therefore the model has been excluded from further considerations.

The SAFT and the Veytsman extensions of the PHSC theory are good for VLE description and prediction of polar systems. Both models give nearly identical results when $\sigma_1 = \sigma_2$. For LLE no definite conclusion is possible now because

- too few systems have been studied theoretically (only systems with one kind of hydrogen bonding either of A-A or A-B type but no systems with two kinds of hydrogen bonds like A-A and A-B in one mixture)
- pure-component parameters are not unique (especially polymer parameters)
- appropriate experimental data are scarce and sometimes of doubtful accuracy

Both extensions are in principle able to describe all observed LLE phase diagrams but quantitative agreement with experimental data is often poor.

Notation

Upper Case

A	Helmholtz energy
A	association site of type *A*
E_{ij}^0	association energy
F_{ij}^0	Helmholtz energy of association
$\mathcal{F}_{a,ij}$	universal function for temperature dependence of a_{ij}
$\mathcal{F}_{b,ij}$	universal function for temperature dependence of b_{ij}
G_{ij}^0	Gibbs energy of association
M_i	total number of association sites on i
N	total number of molecules
N_{AV}	Avogadro's number
N_i	number of molecules of type i
N_{ij}	number of contacts
N_d^i, N_a^j	number of donor / acceptor sites of type i / j
N_{i0}, N_{0j}	number of not bonded donor sites i / acceptor sites j
P	pressure
Q	partition function
R	general gas constant
S_{ij}^0	association energy
T	temperature
U	internal energy
V	volume
V_{ij}^0	association volume
X^{A_i}	fraction of component i which is not bonded to association site *A*
Z	compressibility factor

Lower Case

a_{ij}	v.d.Waals type interaction parameter
a_k^j	number of acceptor sites of type j on molecule k
b_{ij}	size parameter
d_k^i	number of donor sites of type i on molecule k
f_{ij}	fraction of specific interactions
g_{ij}	distribution function
k	Boltzmann's constant
k_{ij}	binary parameter for modification of ε_{ij}
l_{ij}	binary parameter for modification of σ_{ij}
n	number of moles
r	chain length
$\bar{r} = \sum_k x_k r_k$	average chain length
rN	total number of segments
$x_i = n_i / \sum_k n_k$	mole fraction
z_A^i	number of association sites *A* on i

Greek Letters

ε	depth of the pair potential at its minimum
$\phi_i = x_i r_i / \sum_k x_k r_k$	segment fraction
Δ	association strength
η	packing fraction
κ	interaction volume of association
μ	chemical potential
$\nu_{ij} = N_{ij} / rN$	number of hydrogen bonds scaled with total number of segments
$\nu_{i0} = N_{i0} / rN$	number of not bonded donor sites scaled with total number of segments
$\nu_d^i = N_d^i / rN$	number of donor sites scaled with total number of segments
ω	degeneracy factor and entropic penalty for hydrogen bonding
Ω	number of possibilities to distribute N_{ij} hydrogen bonds among N_i donor and N_j acceptor groups
$\rho = N/V$	molecular density
σ	separation distance at the minimum in the pair potential
ζ	reduced density
ψ	probability factor for hydrogen bonding

Superscript, Subscript

A	association site A
a	acceptor
assoc.	association
d	donor
i	component i
PHSC	perturbed hard sphere chain

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Appendix A ($P_{assoc.}$ and $\mu^{assoc.}$ for the SAFT model)

$$\frac{a_{assoc.}}{RT} = \sum_{i=1}^{n} x_i \left[\sum_{A_i}^{m} \left(\ln X^{A_i} - \frac{X^{A_i}}{2} \right) + \frac{1}{2} M_i \right] \tag{A.1}$$

$$X^{A_i} = \left(1 - \sum_{j} \sum_{B_j} \rho_j \cdot X^{B_j} \cdot \Delta^{A_i B_j} \right)^{-1} \tag{A.2}$$

$$\rho_j = x_j \cdot \rho \tag{A.3}$$

$$\Delta^{A_i B_j} = \sigma_{ij}^3 \cdot \kappa_{A_i B_j} \cdot g_{ij}(d_{ij}) \cdot \left[\exp\left(\frac{E^0_{A_i B_j}}{kT} \right) - 1 \right] \tag{A.4}$$

The fraction of non-bonded association sites X^{A_i} is usually given by a system of equations of type 2 and some association-site balance equations. Assuming only one kind of hydrogen bonds (between association site A and B) in a mixture or pure fluid, the general balance equation for any number of association sites of type A and any number of association site B is as follows :

$$z_A^i \cdot x_i \cdot \left(1 - X^{A_i}\right) = z_B^j \cdot x_j \cdot \left(1 - X^{B_j}\right) \tag{A.5}$$

l.h.s. : number of sites A in component i × number of molecules × fraction of non bonded sites = total number of bonded sites.

$$z_A^i \cdot x_i - z_A^i \cdot x_i \cdot X^{A_i} - z_B^j \cdot x_j = -z_B^j \cdot x_j \cdot X^{B_j} \tag{A.6}$$

$$X^{A_i} = \frac{z_B^j \cdot x_j}{z_A^i \cdot x_i} \cdot \left(X^{B_j} - 1\right) + 1 \tag{A.7}$$

$$\begin{aligned} X^{B_j} &= \left(1 - z_A^i \cdot \rho_i \cdot X^{A_i} \cdot \Delta^{A_i B_j}\right)^{-1} \\ &= \left(1 - z_A^i \cdot \rho \cdot x_i \cdot \left[\frac{z_B^j \cdot x_j}{z_A^i \cdot x_i} \cdot \left(X^{B_j} - 1\right) + 1 \right] \cdot \Delta^{A_i B_j} \right)^{-1} \end{aligned} \tag{A.8}$$

$$\left(X^{B_j}\right)^2 \cdot \underbrace{\left(z_B^j \cdot \rho_j \cdot \Delta^{A_i B_j}\right)}_{a} + X^{B_j} \cdot \underbrace{\left(z_A^i \cdot \rho_i \cdot \Delta^{A_i B_j} - z_B^j \cdot \rho_j \cdot \Delta^{A_i B_j} + 1\right)}_{b} - \underbrace{1}_{c} = 0 \tag{A.9}$$

$$X^{B_j} = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \tag{A.10}$$

$$X^{A_i} = \left(1 - z_B^j \cdot \rho_j \cdot X^{B_j} \cdot \Delta^{A_i B_j}\right)^{-1} \qquad \text{A.11}$$

Chemical Potential

$$\frac{A_{\text{assoc.}}}{kT} = \sum_{i=1}^{n} N_i \left[\sum_{A_i}^{m}\left(\ln X^{A_i} - \frac{X^{A_i}}{2}\right) + \frac{1}{2} M_i\right] \qquad \text{A.12}$$

$$\frac{\mu_k^{\text{assoc.}}}{kT} = \left(\frac{\partial A_{\text{assoc.}}/kT}{\partial N_k}\right) \qquad \text{A.13}$$

$$\frac{\mu_k^{\text{assoc.}}}{kT} = \sum_{A_k}\left(\ln X^{A_k} - \frac{X^{A_k}}{2}\right) + \frac{1}{2} M_k + \sum_i \rho_i \sum_{A_i}\left(\frac{1}{X^{A_i}}\frac{\partial X^{A_i}}{\partial \rho_k} - \frac{1}{2}\frac{\partial X^{A_i}}{\partial \rho_k}\right) \qquad \text{A.14}$$

$$\text{with } \left(\frac{\partial}{\partial N_k}\right)_{\text{all } N_i, V, T} = \left(\frac{\partial}{\partial \rho_k}\right)_{\text{all } N_i, V, T} \cdot \underbrace{\left(\frac{\partial \rho_k}{\partial N_k}\right)_{\text{all } N_i, V, T}}_{V^{-1}} \qquad \text{A.15}$$

Differentiation of X^{A_i} (equation A.2) with respect to density of component k yields :

$$\left(\frac{\partial X^{A_i}}{\partial \rho_k}\right)_{\text{all } N_i, V, T} = -\left(X^{A_i}\right)^2 \cdot \left(\sum_{B_k} X^{B_k} \cdot \Delta^{A_i B_k} + \sum_j \sum_{B_j} \rho_i \frac{\partial X^{B_j}}{\partial \rho_k} \Delta^{A_i B_j} + \sum_j \sum_{B_j} \rho_i X^{B_j} \frac{\partial \Delta^{A_i B_j}}{\partial \rho_k}\right) \text{A.16}$$

Assuming that there is only one kind of hydrogen bonding in the mixture, the analytic expressions for X^{A_i} and X^{B_j} can be used to obtain the analytic expressions for the derivatives of X^{A_i} and X^{B_j} with respect to the density of component k. Otherwise k systems of equations have to be solved for all derivatives with respect to ρ_k.

The following differentiations were carried out with all N_i = const., V = const., T = const.

$$\frac{\partial X^{B_j}}{\partial \rho_k} = \frac{u' \cdot v - v' \cdot u}{v^2} \qquad \text{A.17}$$

$$u = -b + \sqrt{b^2 - 4ac} \qquad \text{A.18}$$

$$u' = -\frac{\partial b}{\partial \rho_k} + \frac{1}{2}\left(b^2 - 4ac\right)^{-\frac{1}{2}} \cdot \left(2b\frac{\partial b}{\partial \rho_k} - 4\frac{\partial a}{\partial \rho_k} c\right) \qquad \text{A.19}$$

$$v = 2a \qquad \text{A.20}$$

$$\boldsymbol{v}' = 2\frac{\partial \boldsymbol{a}}{\partial \rho_k} \qquad \text{A.21}$$

$$\boldsymbol{b} = \underbrace{z_A^i \cdot \rho_i \cdot \Delta^{A_i B_j}}_{\boldsymbol{b}_1} - \underbrace{z_B^j \cdot \rho_j \cdot \Delta^{A_i B_j}}_{\boldsymbol{b}_2} + 1 \qquad \text{A.22}$$

$$\frac{\partial \boldsymbol{b}}{\partial \rho_k} = \frac{\partial \boldsymbol{b}_1}{\partial \rho_k} - \frac{\partial \boldsymbol{b}_2}{\partial \rho_k} \qquad \text{A.23}$$

If i=k then

$$\frac{\partial \boldsymbol{b}_1}{\partial \rho_k} = z_A^k \cdot \Delta^{A_k B_j} + z_A^k \cdot \rho_k \cdot \frac{\partial \Delta^{A_k B_j}}{\partial \rho_k} \qquad \text{A.24}$$

else

$$\frac{\partial \boldsymbol{b}_1}{\partial \rho_k} = z_A^i \cdot \rho_i \cdot \frac{\partial \Delta^{A_i B_j}}{\partial \rho_k} \qquad \text{A.25}$$

Calculation of $\frac{\partial \boldsymbol{b}_2}{\partial \rho_k}$ and $\frac{\partial \boldsymbol{a}}{\partial \rho_k}$ is straight forward.

$$\frac{\partial \Delta^{A_i B_j}}{\partial \rho_k} = \sigma_{ij}^3 \cdot \kappa_{A_i B_j} \cdot \frac{\partial g_{ij}}{\partial \rho_k} \cdot \left[\exp\left(\frac{E^0_{A_i B_j}}{kT}\right) - 1\right] \qquad \text{A.26}$$

The derivative of the distribution function g_{ij} with respect to the density of k is described in the appendix for the Veytsman model.

$$X^{A_i} = \underbrace{\frac{z_B^j \cdot x_j}{z_A^i \cdot x_i}}_{\boldsymbol{\partial}_1} \cdot \underbrace{\left(X^{B_j} - 1\right)}_{\boldsymbol{\partial}_2} + 1 \qquad \text{A.27}$$

$$\frac{\partial X^{A_i}}{\partial \rho_k} = \frac{\partial \boldsymbol{\partial}_1}{\partial \rho_k} \cdot \boldsymbol{\partial}_2 + \boldsymbol{\partial}_1 \cdot \frac{\partial \boldsymbol{\partial}_2}{\partial \rho_k} \qquad \text{A.28}$$

$$\frac{\partial \boldsymbol{\partial}_1}{\partial \rho_k} = \frac{\boldsymbol{u}' \cdot \boldsymbol{v} - \boldsymbol{v}' \cdot \boldsymbol{u}}{\boldsymbol{v}^2} \qquad \text{A.29}$$

$$\boldsymbol{u} = z_B^j \cdot x_j \qquad \text{A.30}$$

$$\boldsymbol{u}' = z_B^j \cdot \frac{\partial x_j}{\partial \rho_k} \qquad \text{A.31}$$

$$v = z_A^i \cdot x_i \qquad \text{A.32}$$

$$v' = z_A^i \cdot \frac{\partial x_i}{\partial \rho_k} \qquad \text{A.33}$$

$$x_i = \frac{\rho_i}{\rho} \qquad \text{A.34}$$

$$\text{if i=k then } \frac{\partial x_i}{\partial \rho_k} = \frac{1 - x_k}{\rho} \qquad \text{if i}\neq\text{k then } \frac{\partial x_i}{\partial \rho_k} = -\frac{x_i}{\rho} \qquad \text{A.35}$$

Pressure

$$\frac{A_{\text{assoc.}}}{kT} = V \sum_{i=1}^{n} \rho_i \left[\sum_{A_i}^{m} \left(\ln X^{A_i} - \frac{X^{A_i}}{2} \right) + \frac{1}{2} M_i \right] \qquad \text{A.36}$$

$$\frac{A_{\text{assoc.}}}{kT} = f(\rho_i) \quad \text{with} \quad \rho_i = g_i(V) \qquad \text{A.37}$$

$$\frac{\partial f(\rho_i)}{\partial V} = \sum_i \frac{\partial f}{\partial \rho_i} \cdot \frac{\partial \rho_i}{\partial V} \qquad \text{A.38}$$

$$\begin{aligned} \left(\frac{\partial A_{\text{assoc.}}/kT}{\partial V} \right)_{\text{all } N_i, T} &= \sum_{i=1}^{n} \rho_i \left[\sum_{A_i} \left(\ln X^{A_i} - \frac{X^{A_i}}{2} \right) + \frac{1}{2} M_i \right] \\ &+ V \cdot \sum_k \left\{ \sum_{i=1}^{n} \frac{\partial \rho_i}{\partial \rho_k} \left[\sum_{A_i} \left(\ln X^{A_i} - \frac{X^{A_i}}{2} \right) + \frac{1}{2} M_i \right] + \sum_{i=1}^{n} \rho_i \left[\sum_{A_i} \left(\frac{1}{X^{A_i}} \frac{\partial X^{A_i}}{\partial \rho_k} - \frac{1}{2} \frac{\partial X^{A_i}}{\partial \rho_k} \right) \right] \right\} \cdot \frac{\partial \rho_k}{\partial V} \end{aligned} \qquad \text{A.39}$$

$$\text{If i=k then } \frac{\partial \rho_i}{\partial \rho_k} = 1, \quad \text{if i}\neq\text{k } \frac{\partial \rho_i}{\partial \rho_k} = 0 \qquad \text{A.40}$$

$$\frac{\partial \rho_k}{\partial V} = -\frac{N_k}{V^2} \qquad \text{A.41}$$

Comparison of A.39 with equation A.12 and A.14 shows that

$$\left(\frac{\partial A_{\text{assoc.}}/kT}{\partial V} \right)_{\text{all } N_i, T} = \frac{A_{\text{assoc.}}/kT}{V} - \frac{\sum_k N_k \cdot \mu_k^{\text{assoc.}}/kT}{V} \qquad \text{A.42}$$

$$P_{\text{assoc.}} = -\left(\frac{\partial A_{\text{assoc.}}/kT}{\partial V} \right)_{\text{all } N_i, T} = \frac{\sum_k N_k \cdot \mu_k^{\text{assoc.}}/kT}{V} - \frac{A_{\text{assoc.}}/kT}{V} \qquad \text{A.43}$$

$$Z_{assoc.} = \frac{PV}{n \cdot RT} = \sum_k x_k \cdot \frac{\mu_k^{assoc.}}{kT} - \frac{A_{assoc.}}{kT} \qquad \text{A.44}$$

Appendix B ($P_{assoc.}$ and $\mu^{assoc.}$ for the Veytsman model)

$$\frac{A_{assoc.}}{rN\cdot kT}=\sum_i\sum_j \nu_{ij}\left[1+\frac{F^0_{ij}}{RT}+\ln\frac{\nu_{ij}}{\nu_{i0}\nu_{0j}}-\ln\left(g_{lm}\,\eta\right)\right]+\sum_i \nu^i_d\ln\frac{\nu_{i0}}{\nu^i_d}+\sum_j \nu^j_a\ln\frac{\nu_{0j}}{\nu^j_a} \qquad \text{B.1}$$

$$\nu_{ij}=\frac{N_{ij}}{rN} \qquad \text{B.2}$$

$$\nu_{i0}=\frac{N_{i0}}{rN}, \qquad \nu_{0j}=\frac{N_{0j}}{rN} \qquad \text{B.3}$$

$$\nu^i_d=\frac{N^i_d}{rN}=\frac{\sum\limits_k x_k\cdot d^i_k}{\bar{r}}, \quad \nu^j_a=\frac{N^j_a}{rN}=\frac{\sum\limits_k x_k\cdot a^i_k}{\bar{r}}, \qquad \text{B.4}$$

$$\bar{r}=\sum_k x_k\cdot r_k \qquad \text{B.5}$$

Donor group i is part of component l, acceptor group j is part of component m. Therefore we have to choose distribution function g_{lm} in equation B.1.

In general, the number of hydrogen bonds ν_{ij} is given by a system of equations of type

$$\frac{\nu_{ij}}{\nu_{i0}\cdot\nu_{0j}}=\underbrace{g_{lm}\cdot\eta\cdot\exp\left(-\frac{G^0_{ij}}{RT}\right)}_{\left(B_{ij}\right)^{-1}} \qquad \text{B.6}$$

and some association-sites balance equations.

$$\nu_{i0}=\nu^i_d-\sum_j \nu_{ij} \qquad \text{B.7}$$

Assuming only one kind of hydrogen bonding (only one kind of donor sites in component l and one kind of acceptor site either in component l or m) equations B.6 and B.7 yield a quadratic equation.

$$\nu_{i0}=\nu^i_d-\nu_{ij}, \quad \nu_{0j}=\nu^j_a-\nu_{ij} \qquad \text{B.8}$$

$$B_{ij}=\frac{1}{g_{lm}\cdot\eta}\exp\left(\frac{G^0_{ij}}{RT}\right) \qquad \text{B.9}$$

$$v_{ij}^2 - \underbrace{\left(B_{ij} + v_d^i + v_a^j\right)}_{C_{ij}} + v_d^i \cdot v_a^j = 0 \qquad \text{B.10}$$

$$v_{ij} = \frac{C_{ij}}{2} - \left(\frac{C_{ij}^2}{4} - v_d^i \cdot v_a^j\right)^{0.5} \qquad \text{B.11}$$

Chemical Potential

The general expression for the chemical potential is :

$$\frac{\mu_k^{\text{assoc.}}}{kT} = \left(\frac{\partial A_{\text{assoc.}}/kT}{\partial N_k}\right)_{\text{all } N_i, V, T} \qquad \text{B.12}$$

$$\begin{aligned}
\frac{\mu_k^{\text{assoc.}}}{kT} &= \left(\frac{\partial rN}{\partial N_k}\right)_{\text{all } N_i, V, T} \cdot \left(\frac{A_{\text{assoc.}}}{rN \cdot kT}\right) + rN \cdot \left(\frac{\partial A_{\text{assoc.}}/rN \cdot kT}{\partial N_k}\right)_{\text{all } N_i, V, T} \\
&= r_k \cdot \left(\frac{A_{\text{assoc.}}}{rN \cdot kT}\right) + rN \cdot \left(\frac{\partial A_{\text{assoc.}}/rN \cdot kT}{\partial \rho_k}\right)_{\text{all } N_i, V, T} \cdot \left(\frac{\partial \rho_k}{\partial N_k}\right)_{V,T} \qquad \text{B.13} \\
&= r_k \cdot \left(\frac{A_{\text{assoc.}}}{rN \cdot kT}\right) + \underbrace{\frac{rN}{V}}_{\rho_r} \cdot \left(\frac{\partial A_{\text{assoc.}}/rN \cdot kT}{\partial \rho_k}\right)_{\text{all } N_i, V, T}
\end{aligned}$$

$$\rho_k = \frac{N_k}{V}, \qquad \left(\frac{\partial \rho_k}{\partial N_k}\right)_{V,T} = \frac{1}{V} \qquad \text{B.14}$$

For $V_{ij}^0 = 0$, the derivative of the Helmholtz energy with respect to density of component k can be expressed as follows. For $V_{ij}^0 \neq 0$, the derivative of the exponential part must also be taken into account ($\partial P/\partial \rho_k$).

$$\begin{aligned}
\left(\frac{\partial \frac{A_{\text{assoc.}}}{rN \cdot kT}}{\partial \rho_k}\right)_{\text{all } N_i, T, V} &= \sum_i \sum_j \frac{\partial v_{ij}}{\partial \rho_k}\left[1 + \frac{F_{ij}^0}{RT} + \ln\left(g_{lm} \cdot \eta \cdot \exp\left(-\frac{G_{ij}^0}{RT}\right)\right) - \ln(g_{lm}\,\eta)\right] \qquad \text{B.15} \\
&+ \sum_i \frac{\partial v_d^i}{\partial \rho_k} \ln \frac{v_{i0}}{v_d^i} + \sum_i v_d^i \cdot \frac{\partial \ln \frac{v_{i0}}{v_d^i}}{\partial \rho_k} + \sum_j \frac{\partial v_a^j}{\partial \rho_k} \ln \frac{v_{0j}}{v_a^j} + \sum_j v_a^j \cdot \frac{\partial \ln \frac{v_{0j}}{v_a^j}}{\partial \rho_k}
\end{aligned}$$

For the special case of only one kind of hydrogen bonds, the analytical expression can be derived as follows :

$$\frac{\partial v_{ij}}{\partial \rho_k} = \frac{1}{2}\frac{\partial C_{ij}}{\partial \rho_k} - \frac{1}{2}\left(\frac{C_{ij}^2}{4} - v_d^i \cdot v_a^j\right)^{-0.5} \cdot \left(2C_{ij}\frac{\partial C_{ij}}{\partial \rho_k} - \frac{\partial v_d^i}{\partial \rho_k} \cdot v_a^j - \frac{\partial v_a^j}{\partial \rho_k} \cdot v_d^i\right) \qquad \text{B.16}$$

$$\frac{\partial C_{ij}}{\partial \rho_k} = \frac{\partial B_{ij}}{\partial \rho_k} + \frac{\partial v_d^i}{\partial \rho_k} + \frac{\partial v_a^j}{\partial \rho_k} \qquad \text{B.17}$$

$$\frac{\partial B_{ij}}{\partial \rho_k} = \left(\frac{\partial \frac{1}{\eta}}{\partial \rho_k} \cdot \frac{1}{g_{lm}} + \frac{\partial \frac{1}{g_{lm}}}{\partial \rho_k} \cdot \frac{1}{\eta}\right) \cdot \exp\left(\frac{G_{ij}^0}{RT}\right) \qquad \text{B.18}$$

$$\frac{\partial \frac{1}{\eta}}{\partial \rho_k} = \frac{-\frac{\partial \eta}{\partial \rho_k}}{\eta^2} \qquad \text{B.19}$$

$$\frac{\partial \frac{1}{g_{lm}}}{\partial \rho_k} = \frac{-\frac{\partial g_{lm}}{\partial \rho_k}}{g_{ij}^2} \qquad \text{B.20}$$

Derivative of packing fraction η with respect to density of component k

$$\eta = \frac{\rho}{4}\sum_i x_i \cdot r_i \cdot b_i = \frac{1}{4}\sum_i \rho_i \cdot r_i \cdot b_i \qquad \text{B.21}$$

$$\left(\frac{\partial \eta}{\partial \rho_k}\right)_{\text{all } N_i, V, T} = \frac{1}{4} \cdot r_k \cdot b_k \qquad \text{B.22}$$

Derivative of distribution function g_{lm} with respect to density of component k

$$\frac{\partial g_{lm}}{\partial \rho_k} = \frac{\frac{\partial \eta}{\partial \rho_k}}{(1-\eta)^2} + 1.5 \cdot \frac{\frac{\partial \zeta_{lm}}{\partial \rho_k} \cdot (1-\eta) + 2\frac{\partial \eta}{\partial \rho_k}\zeta_{lm}}{(1-\eta)^3} + 0.5\frac{2\zeta_{lm}\frac{\partial \zeta_{lm}}{\partial \rho_k} \cdot (1-\eta) + 3\frac{\partial \eta}{\partial \rho_k}\zeta_{lm}^2}{(1-\eta)^4} \qquad \text{B.23}$$

Derivative of reduced density ζ_{lm} with respect to density of component k

$$\zeta_{lm} = \left(\frac{b_i \cdot b_j}{b_{ij}}\right)^{1/3} \cdot \frac{\rho}{4}\sum_i x_i \cdot r_i \cdot b_i^{2/3} = \left(\frac{b_i \cdot b_j}{b_{ij}}\right)^{1/3} \cdot \frac{1}{4}\sum_i \rho_i \cdot r_i \cdot b_i^{2/3} \qquad \text{B.24}$$

$$\left(\frac{\partial \zeta_{lm}}{\partial \rho_k}\right)_{\text{all } N_i, V, T} = \left(\frac{b_i \cdot b_j}{b_{ij}}\right)^{1/3} \cdot \frac{1}{4} \cdot \rho_k \cdot b_k^{2/3} \qquad \text{B.25}$$

Derivative of donor / acceptor part with respect to density of component k

- Derivative of total number of donor/acceptor sites v_d^i, v_a^j with respect to number of molecules k

$$v_d^i = \frac{\sum_l N_l \cdot d_l^i}{rN} = \frac{\sum_l x_l \cdot d_l^i}{\sum_k x_k \cdot r_k} = \frac{\sum_l \rho_l \cdot d_l^i}{\sum_k \rho_k \cdot r_k} \qquad \text{B.26}$$

$$\left(\frac{\partial v_d^i}{\partial \rho_k}\right)_{\text{all } N_i, V, T} = \frac{d_k^i \cdot \rho_r - r_k \cdot \sum_l \rho_l \cdot d_l^i}{\rho_r^2} = \frac{d_k^i}{\rho_r} - \frac{r_k \cdot \sum_l x_l \cdot d_l^i}{\bar{r} \cdot \rho_r} \qquad \text{B.27}$$

Equation B.27 becomes for only one kind of hydrogen bonding (donor group in component l) :

$$\left(\frac{\partial v_d^i}{\partial \rho_k}\right)_{\text{all } N_i, V, T} = \frac{d_k^i \cdot \rho_r - r_k \cdot \rho_l \cdot d_l^i}{\rho_r^2} = \frac{d_k^i}{\rho_r} - \frac{r_k \cdot x_l \cdot d_l^i}{\bar{r} \cdot \rho_r} \qquad \text{B.28}$$

- Derivative of logarithmic term

$$\frac{v_{i0}}{v_d^i} = \frac{v_d^i - \sum_j v_{ij}}{v_d^i} = 1 - \frac{\sum_j v_{ij}}{v_d^i} \qquad \text{B.29}$$

$$\frac{\partial \ln \frac{v_{i0}}{v_d^i}}{\partial \rho_k} = \left(1 - \frac{\sum_j v_{ij}}{v_d^i}\right)^{-1} \cdot - \left(\frac{\sum_j \partial v_{ij}}{\partial \rho_k} \cdot v_d^i - \sum_j v_{ij} \cdot \frac{\sum_j \partial v_d^i}{\partial \rho_k}\right) \cdot \left(v_d^i\right)^{-2} \qquad \text{B.30}$$

Pressure

General expression

$$P_{\text{assoc.}} = -\left(\frac{\partial A_{\text{assoc.}}}{\partial V}\right)_{\text{all } N_i, T} \qquad \text{B.31}$$

$$
\begin{aligned}
P_{\text{assoc.}} &= -\left(\frac{\partial rN\cdot kT}{\partial V}\right)_{\text{all } N_i,T}\cdot\left(\frac{A_{\text{assoc.}}}{rN\cdot kT}\right) - rN\cdot kT\cdot\left(\frac{\partial A_{\text{assoc.}}/rN\cdot kT}{\partial V}\right)_{\text{all } N_i,T}\\
&= \quad 0 \quad - rN\cdot kT\cdot\left(\frac{\partial A_{\text{assoc.}}/rN\cdot kT}{\partial \rho}\right)_{\text{all } N_i,T}\cdot\underbrace{\left(\frac{\partial \rho}{\partial V}\right)_{\text{all } N_i,T}}_{-\frac{\rho}{V}} \qquad \text{B.32}\\
&= \underbrace{\frac{rN}{V}}_{\rho_r}\cdot kT\cdot\rho\cdot\left(\frac{\partial A_{\text{assoc.}}/rN\cdot kT}{\partial \rho}\right)_{\text{all } N_i,T}
\end{aligned}
$$

$$
Z_{\text{assoc.}} = \frac{P_{\text{assoc.}}\cdot V}{n\cdot RT} = \frac{P_{\text{assoc.}}}{\rho\cdot kT} = \rho_r\cdot\left(\frac{\partial A_{\text{assoc.}}/rN\cdot kT}{\partial \rho}\right)_{\text{all } N_i,T} \qquad \text{...B.33}
$$

$$
\begin{aligned}
\left(\frac{\partial \dfrac{A_{\text{assoc.}}}{rN\cdot kT}}{\partial \rho}\right)_{\text{all } N_i,T,V} &= \sum_i\sum_j \frac{\partial v_{ij}}{\partial \rho}\left[1+\frac{F_{ij}^0}{RT}+\ln\left(g_{lm}\cdot\eta\cdot\exp\left(-\frac{G_{ij}^0}{RT}\right)\right)-\ln(g_{lm}\,\eta)\right] \qquad \text{B.34}\\
&+\sum_i \frac{\partial v_d^i}{\partial \rho}\ln\frac{v_{i0}}{v_d^i}+\sum_i v_d^i\cdot\frac{\partial \ln\dfrac{v_{i0}}{v_d^i}}{\partial \rho}+\sum_j \frac{\partial v_a^j}{\partial \rho}\ln\frac{v_{0j}}{v_a^j}+\sum_j v_a^j\cdot\frac{\partial \ln\dfrac{v_{0j}}{v_a^j}}{\partial \rho}
\end{aligned}
$$

The derivation of the partial derivatives with respect to density is similar to those with respect to density of component k shown for the chemical potential.

$$
\left(\frac{\partial \eta}{\partial \rho}\right)_{\text{all } N_i,T} = \frac{1}{4}\sum_i x_i\cdot r_i\cdot b_i \qquad \text{B.35}
$$

$$
\left(\frac{\partial \zeta_{lm}}{\partial \rho}\right)_{\text{all } N_i,T} = \left(\frac{b_l\cdot b_m}{b_{lm}}\right)^{1/3}\cdot\frac{1}{4}\sum_i x_i\cdot r_i\cdot b_i^{2/3} \qquad \text{B.36}
$$

$$
\left(\frac{\partial v_d^i}{\partial \rho}\right)_{\text{all } N_i,T} = 0 \qquad \text{B.37}
$$

Appendix C Alkane parameters of PHSC

	r	σ [Å]	ε/k [K]
methane	1.000	4.126	182.1
ethane	1.694	3.916	206.3
propane	2.129	3.998	219.0
butane	2.496	4.085	231.3
pentane	3.149	3.995	226.0
hexane	3.446	4.084	235.6
heptane	4.255	3.947	225.9
octane	5.055	3.850	219.6
nonane	5.748	3.804	217.3
decane	6.616	3.723	212.7
undecane	7.057	3.754	215.4
dodecane	7.712	3.733	214.8
tridecane	7.986	3.794	218.3
tetradecane	9.030	3.682	213.7
pentadecane	9.851	3.662	211.3
hexadecane	10.168	3.703	214.2
heptadecane	10.834	3.680	213.7
octadecane	11.110	3.698	216.5
nonadecane	11.659	3.718	216.1
eicosane	12.925	3.633	212.1