MODIFICATION OF SAKO-WU-PRAUSNITZ EQUATION OF STATE FOR FLUID PHASE EQUILIBRIA IN POLYETHYLENE-ETHYLENE SYSTEMS AT HIGH PRESSURES

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Abstract - In order to model phase equilibria at all pressures, it is necessary to have an equation of state. We have chosen the Sako-Wu-Prausnitz cubic equation of state, which had shown some promising results. However, in order to satisfy our demands, we had to modify it slightly and fit new pure component parameters. New pure component parameters have been determined for ethylene and the *n*-alkane series, using vapor pressure data, saturated liquid volume and one-phase PVT-data. For higher n-alkanes, where vapor pressure data are poor or not available, determination of the pure component parameters was made in part by extrapolation and in part by fitting to one-phase PVT-data. Using one-fluid van der Waals mixing rules, with one adjustable interaction parameter, good correlation of binary hydrocarbon system was obtained, except for the critical region. The extension of the equation of state to polyethylene systems is covered in this work. Using the determined parameters, flash and cloud point calculations were performed, and treating the polymer as polydisperse. The results fit data well.
Keywords: Polyethylene-ethylene systems; Phase behavior.

INTRODUCTION

In the production of polyethylene, phase behavior is important for three different reasons. First, ethylene polymerization should take place in a homogeneous fluid phase since the reaction rate and subsequent product quality is easier to control if the fluid remains in a single phase (de Loos *et al.*, 1983, 1996). Second, industrial processes to produce polyethylene are continuous, requiring the polymer-solvent mixture to remain a homogeneous fluid until it reaches the separation stage. Flow problems result if the mixture separates early because the polymer-rich phase has high viscosity. Third, separation of unreacted ethylene is accomplished by purposely

bringing the polymer-solvent mixture into the multi-phase region. The average molecular weight, molecular weight distribution and branch density all influence polymer-solvent phase behavior (Chan *et al.*, 2000). Cloud points in polyethylene-ethylene systems have been experimentally determined for different types of polyethylene. High density polyethylene (HDPE)-ethylene systems were investigated by (de Loos 1981, Rousseaux *et al.*, 1985, Nieszporek, 1991). Low density polyethylene (LDPE)-ethylene systems were investigated by (Swelheim *et al.*, 1965, Steiner and Horle, 1972, Cheng and Bonner, 1977, Rätzsch *et al.*, 1980, Spahl and Luft, 1981, 1983, 1986, Wohlfarth *et al.*, 1981, Kobyakov *et al.*, 1987, Nieszporek, 1991,

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Heukelbach and Luft, 1993,1996., de Loos *et al.*, 1995, Muller, 1996, Horst *et al.*, 1998, Dietzsch, 1999, Beyer *et al.*, 2002, Buback and Latz, 2003, Trumpi et al., 2003 Becker *et al.*, 2004, Davis *et al.*, 2004). Systems of ethylene and different linear copolymers of polyethylene have also been examined (Heukelbach and Luft, 1993, Gregg *et al.*, 1993, Chan *et al.*, 2000).

Various equations of state have been proposed and modified to predict polymer-solvent phase behavior. A few of the more common are the Sanchez-Lacombe model (Sanchez and Lacombe 1976, 1978), the Kleintjens-Koningsveld Mean-Field Lattice Gas model (Kleintjens and Koningsveld, 1980), the Perturbed Hard-Sphere Chain model (Song *et al.*, 1994a, 1994b, 1996), and the Statistical Associated Fluid Theory (SAFT) (Wertheim, 1987., Huang and Radosz, 1991).

The first attempt to apply a cubic equation of state in polymer solutions has been made by (Sako *et al.*, 1989), introduced a three-parameter cubic equation of state, where apart from the energy a, and co-volume b, parameters, Prigogine's external degrees of freedom parameter c is employed for the extension of the equation to polymers. However, the evaluation of these parameters is quite complicated for both the solvent and the polymer and thus, this approach can not retain the simplicity of a cubic equation of state.

On the other hand, (Kontogeorgis *et al.*, 1994) proposed the use of van der Waals equation of state with a very simple method for the calculation of the attractive and repulsive parameters of the equation of state. According to this method, the parameters a and b of polymer are fitted to two experimental volumetric data at essentially zero pressure. The extension to polymer solution was achieved by using the classical van der Waals one fluid mixing rule, the arithmetic mean combining rule for b_{ij} and the Berthelot one for a_{ij} with one binary interaction parameters, l_{ij}. In a series of papers, this approach was applied with satisfactory results to: (1) the correlation and prediction of VLE (Kontogeorgis *et al.*, 1994, Harismiadis *et al.*, 1994a); (2) the correlation and prediction of LLE in polymer solutions and blends (Harismiadis *et al.*, 1994b, 1996, Saraiva *et al.*, 1996); and (3) the correlation and prediction of Henry constants (Bithas *et al.*, 1996).

(Orbey and Sandler, 1994), fitted the two parameters of the PRSV equation of state for the pure polymer to its volumetric data at the temperature range of interest by assuming that its vapor pressures equal to 10^{-7} MPa. In order to

correlate the VLE in polymer solutions, they employed the mixing rule proposed by (Wong and Sandler, 1992) by coupling the equation of state FH G^E model, and employing two binary interaction parameters, k_{ij} and χ (Flory interaction parameter).

In this work we first modify the Sako-Wu-Prausnitz by the idea that increasing in carbon number of the n-alkanes causes a regular change in the parameters of equation of state and critical properties. Then with this procedure the parameters of this modified equation of state is estimated for heavy n-alkanes and polyethylene. Finally the phase equilibrium calculations perform.

THEORY

The Sako-Wu-Prausnitz (SWP) equation of state was developed by (Sako *et al.*, 1989) and contains one more parameter than the better known Soave-Redlich-Kwong (SRK) equation of state. This parameter, called c, is a measure of the number of external rotational and vibrational degrees of freedom, which makes the equation of state suitable for systems containing large molecules. The equation of state is a member of the cubic family:

$$P = \frac{RT(v - b + bc)}{v(v - b)} - \frac{a(T)}{v(v + b)} \tag{1}$$

Like in the van der Waals equation of state, the parameter a accounts for the attractive forces between the molecules and parameter b is a measure of the molecular size. The c parameter is already mentioned, and the connection to SRK is obtained by setting $c = 1$, which is also the minimum physical limit for c. The equation of state parameters, are related to the critical point, using the classical definition:

$$\left(\frac{\partial P}{\partial v}\right)_{T=T_c} = 0 \tag{2}$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_c} = 0 \tag{3}$$

where subscript c means at the critical point. Using the conditions (2) and (3) on the equation of state, (1), the following relations at the critical point are obtained:

$$a_c = \frac{(1 + D_0)^3}{18 D_0} \frac{R^2 T_c^2}{P_c} \tag{4}$$

$$b_c = \frac{D_0}{3}\frac{RT_c}{P_c} \qquad (5)$$

$$c_c = \frac{(1-D_0)^3}{6D_0^2} \qquad (6)$$

$$v_c = \frac{1}{3}\frac{RT_c}{P_c} \qquad (7)$$

where D_0 is an adjustable parameter. The reason of why D_0 suddenly pops up is purely mathematical. We have a system of 3 equations, (1), (2) and (3) which we solve with respect to four variables, a_c, b_c, c_c and v_c. This means that three of the variables must be a function of the fourth one. Here we have introduced D_0 for pure convenience, instead we could have for instance made a_c and c_c functions of b_c. The relations are the same as those obtained by (Sako *et al.*, 1989), however Eq. (4) is simplified.

The result in Eq. (7) lead to a constant value of the critical compressibility factor:

$$Z_c = \frac{P_c v_c}{RT_c} = \frac{1}{3} \qquad (8)$$

Typical experimental values for the critical compressibility factor are 0.26-0.29 for *n*-alkanes up to octane (Poling *et al.*, 2001) which means that deviations from experimental data are expected around the critical point. At temperatures other than the critical one:

$$a(T) = a_c.\alpha(T) \qquad (9)$$

$$b = b_c \qquad (10)$$

$$c = c_c \qquad (11)$$

(Sako *et al.*, 1989) presented equation of state parameters for the n-alkane series, ethylene and polyethylene, and their results for an ethylene–polyethylene system looked promising. However, (Gregg *et al.*, 1993) compared the SWP equation of state with the SRK equation of state and the statistical associating fluid theory (SAFT, Huang and Radosz, 1990, 1991) for a number of ethylene+n-alkane systems, and it turned out that the SWP equation of state had the poorest agreement with the experimental data. This was surprising since SWP contains one more parameter than SRK, and should thereby produce equal or better results. There might be several reasons for this result, the obvious one is

that there might be something wrong with the pure component parameters, and it motivated us to look further into this.

For the parameter a, (Sako *et al.*, 1989) used one empirical temperature function for volatile fluids and for polymers they determined the temperature function from London's formula for dispersion forces. In this work we have used the Soave temperature function:

$$\alpha(T) = (1 + f(1 - \sqrt{T_r}))^2 \qquad (12)$$

where f is a compound dependent parameter fitted to experimental vapor pressure and PVT-data.

Evaluation of Pure Component Parameters

Before we can use the equation of state for calculating phase equilibria for mixtures, we need to determine the pure component equation of state parameters. In our case we have a total of four parameters to be determined: D_0, T_c, P_c and the Soave parameter f. Pure component parameters for volatile compounds are typically determined using saturated properties and relating the parameters to the critical point, which for us means that we set T_c and P_c to the experimental critical values and fit D_0 and f to vapor pressure data. However, polymers do not have a measurable saturated pressure and decompose long before reaching the critical point, so the only data available is one phase PVT-data. For calculation of phase equilibria using an equation of state, it is always preferable that the pure component equation of state parameters, are determined from vapor pressure data. Fitting all four parameters directly to PVT-data, give a very good fit, but poor phase equilibria. Since polyethylene strictly speaking is a very large alkane, it should be possible to extrapolate some of the parameters from an alkane-series, and fit the remaining to PVTdata.

Selection of Experimental Data Points

It is always an advantage to test experimental data which is to be used in parameter estimation in models. If we use bad data for optimization of parameters in our model, the model will likely produce poor results.

Test of vapor pressure data is typically performed graphically, and one of the most common ones is to plot $\ln(P)$ as a function of $1/T$. The resulting curve should then be linear for "good" data, while "bad" data should be off the linear curve. The theoretical foundation for

this linearity was established in the 19th century by Clapeyron and Clausius (Poling *et al.*, 2001).

In this work first, we collected a databank of experimental vapor pressure data, and then, we performed vapor pressure graphical test which, was explained. After performing this graphical test, the best experimental vapor pressure data were selected graphically in compare of other data and, the pure PVT-Data collection was added to this databank (The references of this databank are available from the authors).

Pure Component Parameters

Pure component parameters are fitted to saturated vapor pressure, PVT-data and saturated liquid densities, whichever available, using a least square routine. The following objective function has been used:

$$O = \frac{w_p^{vap}}{n_p^{vap}} \sum_i^{n_p^{vap}} (1 - \frac{P_{calc}^{vap}}{P_{exp}^{vap}})^2 + \frac{w_v^{liq}}{n_v^{liq}} \sum_i^{n_v^{liq}} (1 - \frac{v_{calc}^{liq}}{v_{exp}^{liq}})^2 \qquad (13)$$

where w is a weighting factor, P^{vap} is the vapor pressure, v^{liq} is the saturated liquid volume and n is the number of experimental points. Subscripts calc and exp mean calculated and experimental,

respectively. The following weights have been used throughout in the optimization:

$$w_p^{vap} = 3$$

$$w_v^{liq} = 1$$

Pure component parameters were determined by fitting the D_0 parameter in Eqs. (4)-(6) and the temperature function parameter f in Eq. (12) to the vapor pressure data and saturated liquid volumes and to the PVT-data. Values for the critical temperature and critical pressure for n-alkanes were those recommended by (Ambrose and Tsonopoulos, 1995) and for ethylene those recommended by (Tsonopoulos and Ambrose, 1996). The results are summarized in Table 1.

Figure 1 shows the fitted D_0 and f parameters plotted against the carbon number for alkanes $C_1 - C_{17}$. The scattering is expected, due to inaccuracies in experimental data used in the fitting process, but apart from this the parameters behave well. The D_0 parameter is clearly a decreasing function with increasing carbon number, while the f parameter is an increasing function with carbon number. However, neither D_0 or f is a linear function, making extrapolation difficult and hazardous.

Table1: Obtained results for first seventeen n-alkanes by optimization of experimental data (Gharagheizi, 2005).

|						%AD	
Component	**T Range**	**D_0**	**f**	**T_c**	**P_c**	**P^{vap}**	**v^{liq}**
Methane	90.69-620	0.2599	0.4863	190.56	4.599	1.33	5.41
Ethane	89.89-625	0.2445	0.5509	305.32	4.872	1.77	3.35
Propane	89.98-600	0.2342	0.5779	369.83	4.248	2.59	5.7
Butane	134.86-660	0.2246	0.602	425.12	3.796	2.89	3.05
Pentane	143.45-650	0.2238	0.657	469.7	3.37	2.71	3.18
Hexane	174.75-663.15	0.2102	0.6469	507.6	3.025	2.94	2.2
Heptane	182.56-573.15	0.2063	0.6908	540.2	2.74	3.29	3.02
Octane	216.37-623.15	0.2047	0.7257	568.7	2.49	3.21	0.36
Nonane	223.15-573.15	0.2013	0.7677	594.6	2.29	2.57	0.84
Decane	243.50-700.00	0.193	0.7492	617.7	2.11	3.68	1.1
Undecane	253.15-523.15	0.1975	0.8468	639	1.98	3.41	2.64
Dodecane	263.67-588.13	0.1893	0.817	658	1.82	4.05	2.8
Tridecane	273.65-573.15	0.1827	0.8095	675	1.68	3.82	2.19
Tetradecane	279.01-588.13	0.1794	0.8124	693	1.57	3.22	3.3
Pentadecane	293.83-576.95	0.1778	0.8404	708	1.48	4.04	2.55
Hexadecane	291.55-593.85	0.1747	0.8455	723	1.4	4.78	2.19
Heptadecane	295.15-610.15	0.1731	0.8713	736	1.34	4.15	1.8
Ethylene	79.45-450.00	0.2437	0.5376	282.34	5.041	0.78	2.01
[a] Average Deviation : $\%AD = \frac{1}{100n} \sum_i^n \left| \frac{S_{exp} - S_{calc}}{S_{exp}} \right|$ where S is given property.							
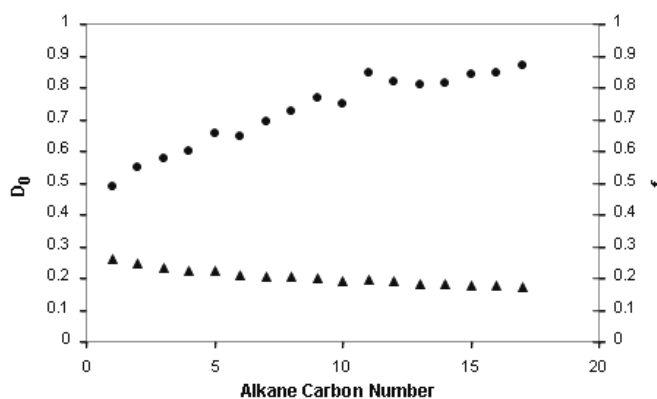
Figure 1: Change of D_0 and f with carbon number for first seventeen n-alkanes

Converting D_0 to a_c, b and c, using Eqs. (4)- (6), gives much simpler correlations. Figure 2 to Figure 4, shows the equation of state, parameters a_c, b and *c* plotted against increasing alkane carbon number. While ac shows a quadratic dependence with respect to carbon number, b and *c* show a linear dependence, making them our choices for extrapolation. For alkanes higher than C_{17}, parameters b and c are extrapolated in the form of Eqs. (14), (15).

$$b = 18.81cn + 11.655 \qquad (14)$$

$$c = 0.1314cn + 0.9552 \qquad (15)$$

where cn is the alkane carbon number. Parameters a_c and f are fitted to the vapor pressure data and saturated liquid volumes and to the PVT-data. The results are shown in Table 2.

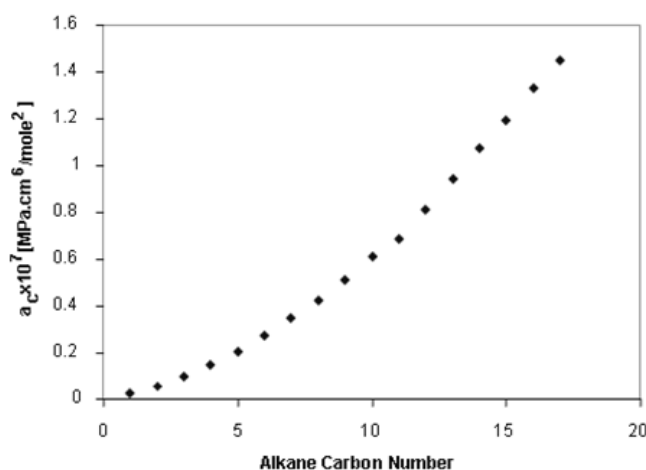The critical properties are calculated from the values of a_c, b and c, using Eqs. (4)- (6).

Figure 2: Equation of state parameter a_c plotted as a function of increasing alkane carbon number
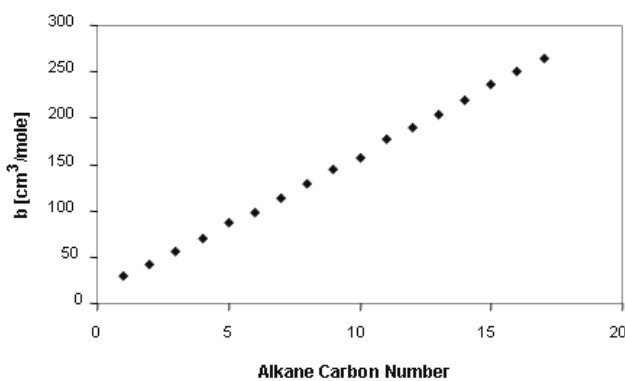

Figure 3: Co-volume parameter b plotted as a function of increasing alkane carbon number
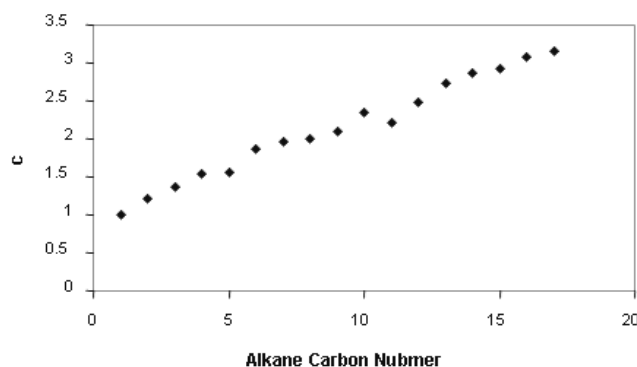
Figure 4: Parameter c plotted as a function of increasing alkane carbon number

**Table 2: Obtained results for heavy n-alkanes and waxes by
optimization of experimental data (Gharagheizi, 2005).**

Component	T Range	$a_c \cdot 10^6$ $\left[\dfrac{Mpa.cm^6}{Mole^2} \right]$	f	b cm3	c	AD [%] P^{vap}	v^{liq}
Octadecane	301.35-593.15	16.219	0.8382	278.235	3.3204	2.63	3.32
Nonadecane	313.15-613.15	17.751	0.8498	293.045	3.4518	3.18	1.7
Eicosane	313.15-625.99	19.405	0.8483	307.855	3.5832	1.76	1.84
Docosane	323.08-573.13	22.715	0.8745	337.475	3.846	3.61	na*
Tetracosane	333.52-588.13	26.575	0.8543	367.095	4.1088	2.53	na*
Hexacosane	379.15-529.65	30.571	0.8622	396.715	4.3716	2.71	na*
Octacosane	453.15-588.13	34.484	0.8902	426.335	4.6344	1.34	na*
Triacontane	373.15-573.15	40.32	0.9136	456.186916	4.8951	na*	0.98
Tetracontane	423.15-573.15	67.031	0.9496	604.324581	6.209	na*	1.01
Octaheptacontane	410.71-518.15	210.49	1.0253	1166.91895	11.2103	na*	0.98
Pentacontahectane	420.05-517.45	721.42	1.0877	2233.79345	20.6674	na*	0.81

* Vapor pressures are not available.

For alkanes higher than C_{28} vapor pressure data are either very poor or not available at all. For these alkanes only one-phase PVT data has been used. We could try to use the same recipe as for the alkanes from $C_{18} - C_{28}$, however it turns out that the f parameter drops in value to about 0.75 for triacontane. The f parameter should be an increasing function of the carbon number, due to the increase of the critical temperature. The cause of this might be the lack of vapor pressure data in the fit. This means that we need to extrapolate one more parameter for the alkanes which do not have reliable vapor pressure data. The only two left are a_c and f, so let us have a close look on them both. Figure 5 shows that the attractive parameter a_c is quadratically dependent on the alkane carbon number, as expected. However, extrapolating quadratic functions should be avoided, since possible errors also increase quadratically.

$$a_c = 3.608 \times 10^4 cn^2 + 2.556 \times 10^5 cn - 8.964 \times 10^4 \quad cn < 18$$

$$(16)$$

$$a_c = 0.0287 \times 10^4 cn^2 + 0.544cn - 5.732, \quad cn > 18$$

Figure 6 shows that the f parameter might be extrapolated using a three parameter correlation. Even if we have more scattering of the f parameter than for the a_c parameter, we choose to extrapolate the f parameter. Possible errors will be much higher for the quadratic correlation, than for the correlation of f and this is especially important when we plan to extrapolate all the way to polyethylene.

$$f = \frac{cn}{-0.51895 + 1.8731\sqrt{cn} + 0.76989cn} \quad (17)$$

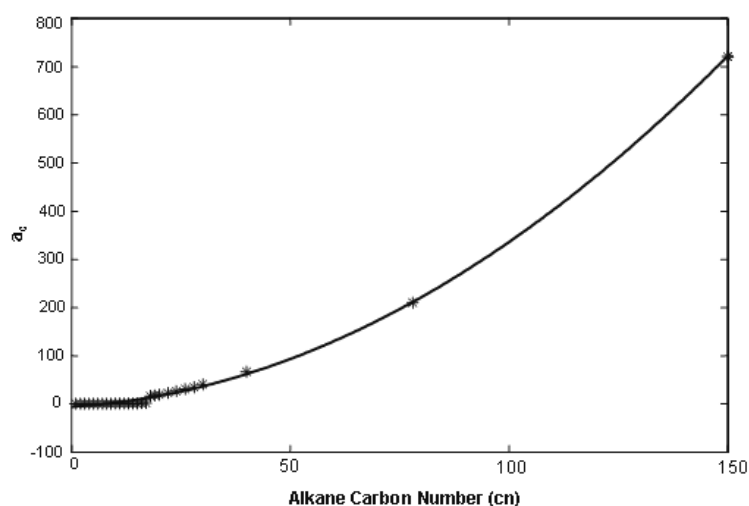For alkanes higher than C_{28}, parameter b, c, a_c and f are extrapolated, using Eqs. (14)- (17).

Figure 5: Attraction parameter a_c plotted as a function of alkane carbon number
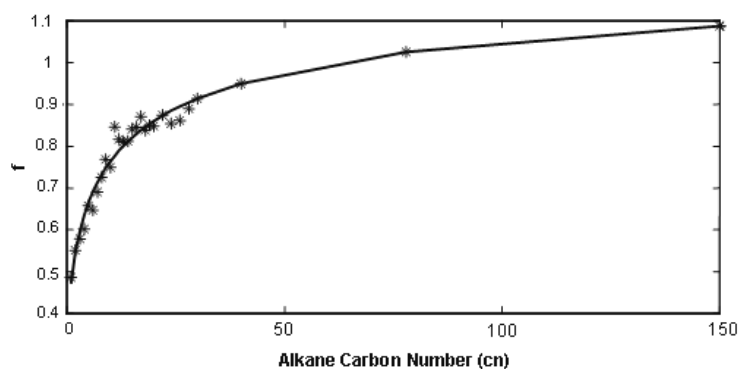

Figure 6: Attraction parameter f plotted as a function of alkane carbon number

Binary Mixtures

As (Sako *et al.,* 1989) did, we assume one-fluid mixing rules, for fluid phase equilibria for multicomponents mixtures.

$$a_m = \sum_i \sum_j x_i x_j a_{ij}(1 - k_{ij})$$

$$b_m = \sum_i x_i b_i \qquad (18)$$

$$c_m = \sum_i x_i c_i$$

where subscript *m* means mixture property and subscript *i* means component property. k_{ij} is an interaction parameter, which is typically fitted to phase equilibria data.

The derivation of the fugacity coefficient for component i by an equation of state is described in detail in (Poling et al., 2001).

Phase equilibria for binary mixtures were calculated. The principle of maximum likelihood has been used for calculation of the error. Experimental phase equilibria data consist of vapor and, or liquid composition at given pressure and temperature. We assume that the experimental temperature data are the most accurate and therefore keep *T* constant while minimizing the following objective function for each experimental point:

$$O = \left(1 - \frac{P_{calc}}{P_{exp}}\right)^2 + \left(1 - \frac{x_{calc}}{x_{exp}}\right)^2 + \left(1 - \frac{y_{calc}}{y_{exp}}\right)^2 \qquad (19)$$

where subscript *calc* means calculated property and exp means experimental property. In Eq. (19) one needs to optimize with respect to one of the

properties, while calculating the two others. For instance, optimizing P_{calc} leads to a PT-flash calculation of the vapor and liquid compositions. The reason for choosing the maximum likelihood method is to avoid large deviation of the calculated composition from the experimental composition in cases where the composition varies much over a small pressure range.

For optimizing the interaction parameter, k_{ij}, we use the same maximum likelihood principle. In the objective function we now need to sum over all the included data points:

$$O_{k_{ij}} = \sum_{i}^{n_{exp}}\left(1 - \frac{P_{calc}}{P_{exp}}\right)^2 + \sum_{i}^{n_{exp}}\left(1 - \frac{x_{calc}}{x_{exp}}\right)^2 + \\ + \sum_{i}^{n_{exp}}\left(1 - \frac{y_{calc}}{y_{exp}}\right)^2 \qquad (20)$$

Table 3 shows results of selected hydrocarbon binary systems and lists temperature and pressure ranges, optimized k_{ij} values (if not set equal to zero), number of points used in fitting, average deviations in pressure and liquid and vapor phase composition.

Table 3: Binary hydrocarbon systems (experimental data from de Loos et al. (1984)).

					%AD	
System	**T [K]**	**P [MPa]**	**k_{ij}**	**No. pts**	**P**	**x**
Ethylene+						
Eicosane	323-423	0.49-24.40	0.0211	88	1.31	1.29
Hexacosane	348-448	0.78-30.18	0.0232	121	1.62	2.32
Trtracontane	348-448	1-30.4	0.0251	45	1.8	2.01
Tetracontane	373-448	0.9-40.56	0.0293	90	1.21	1.64

Phase Equilibria in Polyethylene+Ethylene Systems

In phase equilibria calculations, there are in general two ways to account for the molecular weight distribution of the polymer; the use of continuous thermodynamics and of pseudocomponents. Both procedures involve the use of a theoretical distribution function to represent the actual molecular weight distribution. In the continuous thermodynamics approach, the theoretical distribution function is used directly instead of mole fractions in the phase equilibria calculations, while in the pseudocomponents approach, the theoretical distribution function is divided into a number of discrete pseudocomponents, each with a given molar mass and mole fraction. Several methods on how to divide the theoretical distribution exists. (Sako *et al.*, 1989) used the Laguerre-Gaussian quadrature method. This procedure is an integration method which, by the use of orthogonal polynomials, divides the function into n optimal parts.

In this work we used from the procedure, which used by (Sako *et al.*, 1989), for calculation of pseudocomponents. Table 4 shows the results of this procedure for the system which presented by (Trumpi *et al.*, 2003). In this work we used 16 pseudocomponents for polyethylene.

Pure component equation of state parameters of polyethylene pseudocomponents were determined by eqs. (14) - (17). In this work, we assumed that any polyethylene pseudocomponents, is a large n- alkanes.

In this paper we select the system of polyethylene-ethylene described experimentally by (Trumpi *et al.*, 2003). The average molecular weights and the pseudocomponents in this calculation are shown in Table 4.

The results for this system containing cloud points and shadow points curves are shown in Figure 5 in comparing with experimental data.

Obtained results for k_{ij}, show the linear dependency with temperature. The k_{ij} parameter for this system, is in the form of

$$k_{ij} = -0.000406\ T + 0.137989 \qquad (21)$$

**Table 4: Characterization of Polyethylene (Trump et al. 2003) and
Assumed 16 Pseudocomponents in this calculation.**

Molar Fraction and Molecular Weights of 16 Pseudo components ($M_n=48000$, $M_w=52000$)			
Mole Fraction	**Molecular Weight**	**Mole Fraction**	**Molecular Weight**
9.393183e-010	7065.215	0.2467892	51449.53
5.916796e-007	9805.932	0.1094475	64100.24
5.240349e-005	12936.35	0.02615174	80112.38
0.001399687	16650.28	0.003197568	100695.7
0.01524479	21120.75	0.000182454	127731.8
0.07891863	26547.32	4.123473e-006	164402.6
0.2114485	33178.8	2.675124e-008	216886
0.3071628	41337	2.204668e-011	301019.7
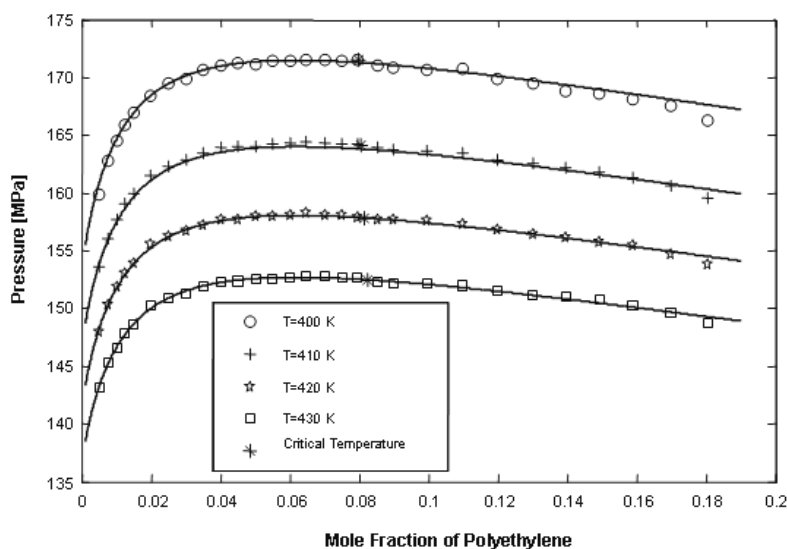
Figure 7: Isotherms of Polyethylene+Ethylene with k_{ij} in Eq. (21).
Correlation from Equation of State with 16 Pseudocomponents.

CONCLUSION

The Sako-Wu-Prausnitz equation of state was modified and extended to polyethylene. Pure component parameters for polyethylene were determined from a combination of extrapolation and fitting. The parameters a_c, b, c, and f were extrapolated from the results obtained by pure parameter fitting of the n-alkane series. Using the determined parameters, flash and cloud point calculations were performed, treating the polymer as polydisperse.

This modified equation of state enables us to modeling the phase behavior of all systems in the form of n-alkanes+ethylene. The same approach can be used for phase behavior of systems in the form of n-alkanes+any components. Advantage of this method is the facility of application of this equation of state for studying of phase behavior of systems.

On the other hand, the strategy of gradual change of parameters of equation of state can be used for other components homologues such siloxanes and other components that the experimental data for their systems are available in the literature for number of the repeating units. Even this strategy can be used for other physical properties in the science and engineering.

NOMENCLATURE

α	Temperature Dependent Part of a	(-)
a	Attractive Parameter	(MPa.cm^6/mole^2)
b	Co-Volume Parameter	(cm^3)
c	Parameter of Equation of State	(-)
cn	Alkane Carbon Number	(-)

D_0	Derived Parameter in Sako-Wu-Prausnitz Equation of State	(-)
f	Temperature Function Prameter	(-)
k_{ij}	Interaction Parameter	(-)
M_n	Number-average Molecular Weight	(gr/mole)
M_w	Mass-average Molecular Weight	(gr/mole)
O	Objective Function	(-)
P	Pressure	[MPa]
P_c	Critical Pressure	(MPa)
P^{vap}	Vapor Pressure	(MPa)
R	Gas Constant	(-)
T	Temperature	(K)
T_c	Critical Temperature	(K)
v	Molar Volume	$(cm^3/mole)$
v^{liq}	Liquid Molar Volume	$(cm^3/mole)$

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