

THE PERTURBED HARD CHAIN THEORY FOR THE PREDICTION OF SUPERCRITICAL FLUID EXTRACTION: PURE COMPONENT PROPERTIES

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Abstract—A perturbed hard chain theory based equation of state is investigated in view of its application to supercritical fluid extraction process calculations. The investigation is focused on pure component properties, since it is essential for any equation to give a good description of volumetric and equilibrium properties of pure compounds before extending it to mixtures. The equation gives good results as far as the correlation of polar and non-polar fluids is concerned. Generalized correlations of the equation parameters are established in terms of Bondi's volume. Their applicability is evaluated on components not included in the data base for the parameter estimation. The results obtained are fairly good, showing that the generalized correlations are convenient specifically for those compounds for which experimental data are difficult to measure. A procedure is proposed to reduce the equation to a one-parameter equation without losing accuracy. The single parameter is calculated from vapor pressure datum.

INTRODUCTION

Supercritical fluid extraction (SFE) is a process in which the solvent is a gas above its critical temperature and at high pressure. Over 100 years ago it was found (Hannay and Hogarth, 1879) that solvents in such conditions have enhanced solubility characteristics. Extensive research on that process started after the first successful industrial application to the decaffeination of green coffee beans (Eisenbach *et al.*, 1983). A very important role in separation process design is played by the description of phase equilibria: an example of thermodynamic equilibrium calculation procedure for process design was given by Starling *et al.* (1985). Equation-of-state (EOS) based methods have been used for modeling phase diagrams, dependence of vaporized fraction on pressure, and temperature and pressure effect on mole fraction of heavy components in the vapor phase. Moreover, the same method may be used to predict the influence of pressure on solvent recovery or selectivity with respect to the separation of heavy components. In all these calculations it is important to know, with good accuracy, not only the vapor pressure but the liquid and vapor density as well. The importance of having a reliable equation of state is evident.

In selecting an EOS for the use in SFE, one should keep in mind a peculiar and essential feature of the systems involved in such separation processes, namely the big difference in size of the molecules. The equations based on the perturbed hard chain theory (PHCT) properly account for differences in size and

shape of the molecules. Additionally, the PHCT equation parameters have a physical significance which is rather important for their estimation and prediction. Finally the critical conditions, whose knowledge is doubtful for many compounds of interest in SFE, are not needed using such a model.

The PHCT equation of state is an extension of the van der Waals theory and is based on Prigogine and Flory theories for dense fluids. The first equation of this type was developed by Beret and Prausnitz (1975). The equation was later modified by Donohue and Prausnitz (1978). The version considered in this work is the one proposed by Cotterman *et al.* (1986). The characteristic of the equation is the low-high density split. This split is of particular importance for mixtures of interest in SFE processes: in fact at the critical density of hexadecane the relative contribution from the high density limit is much larger than that from the low density limit, but at the critical density of methane or carbon dioxide the two contributions are nearly identical.

The scope of this work is then to investigate the description of pure component saturation properties (VLE) and supercritical behavior (PVT) and the predictive capabilities of the Cotterman *et al.* EOS for high molecular weight substances.

EQUATION OF STATE

The perturbed hard chain theory equation of state derived by Cotterman *et al.* is based on the generalized van der Waals theory. The residual Helmholtz energy may be written in the following form:

$$a^r = a^{ref} + a^{pert} \quad (1)$$

where a^{ref} is the reference or repulsive term and a^{pert} is the perturbation or attractive term.

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The reference term is assumed to be described by the hard-sphere Carnahan–Starling (1972) equation. The perturbation part of the equation is developed on the basis of Gubbins and Twu theory (1978). The formulae for the attractive part of the residual Helmholtz energy are quite involved and can be found in the original paper (Cotterman *et al.*, 1986).

In this model each pure substance is characterized by three molecular parameters: v^* , T^* and c . The soft core molar volume is defined as:

$$v^* = \frac{r\sigma^3 N_{av}}{\sqrt{2}} \quad (2)$$

where r is the number of segments, σ is the soft core diameter of one segment and N_{av} is Avogadro's number. The constant T^* is defined as:

$$T^* = \varepsilon q / ck \quad (3)$$

where $\varepsilon q/k$ is the potential energy per molecule, ε is the potential energy per unit surface area and k is Boltzmann's constant. Parameter c is the number of external degrees of freedom (Prigogine, 1957): a measure of flexibility and asymmetry of the molecule.

For polar substances the dipole and quadrupole moments (μ , Q) are also included in the model. These values appear in the attractive term of the equation of state and, as a first approximation, they could be set to zero if no experimental data are available.

CALCULATION PROCEDURE

A parameter estimation program has been developed, with particular attention given to the numerical aspects in order to minimize the CPU time and to improve the precision. Such aspects become particularly important when one is dealing with rather complicated equations of state, such as the one considered in this work.

The density calculation procedure employed is the one proposed by Topliss *et al.* (1988). The numerical precision in the density calculation routine for very low pressures was not sufficient to give satisfactory results in the parameter estimation, so we restricted the reduced pressure data to be $> 5 \times 10^{-4}$.

Calculation of pure-component vapor pressures for a given temperature involves the solution of the thermodynamic equilibrium condition given by the following equation:

$$\phi^L(T^{exp}, P) = \phi^V(T^{exp}, P) \quad (4)$$

or:

$$F(P) = \ln \phi^V(T^{exp}, P) - \ln \phi^L(T^{exp}, P) = 0 \quad (5)$$

where T^{exp} is an experimental temperature and ϕ^L , ϕ^V are the fugacity coefficients of the equilibrium liquid and vapor phase, respectively. Many possibilities are available for solving this equation with respect to P . Among the others we have selected the method described by Van Ness and Abbott (1982) reported in Appendix A.

It is essential to use a parameter search procedure which ensures good results for the parameters and a

reasonable computational time. The procedure becomes dramatically important in the case of parameters which are strongly correlated (like Q with T^* and c). Particular care has been given to the objective function used in the parameter estimation. The objective function used in this work is the following (see Appendix B for details on the derivation):

$$OF = \sum_i^n [\ln \phi^V(P^{exp}) - \ln \phi^L(P^{exp})]^2 + \sum_i^n \left[\frac{(V_L^{exp} - V_L^{calc})}{V_L^{exp}} \right]^2 + \sum_j^m \left[\frac{(V^{exp} - V^{calc})}{V^{exp}} \right]^2 \quad (6)$$

where ϕ is the fugacity coefficient, V_L is the saturated liquid volume, V is the fluid volume for PVT data, n is the number of VLE data points ($T < T_c$) and m is the number of PVT data points. Using this objective function one should be aware that each vapor pressure data point is weighted by the $(Z^V - Z^L)$ term, i.e. a lower weight is given to the points at higher pressures where the $(Z^V - Z^L)$ term is smaller [see eq. (A2)].

A robust method for the optimization of an objective function given as a sum of squares is the one proposed by Marquardt (1963). Two numerical procedures implementing this method have been compared in this work. The first was written by Fletcher (Harwell's subroutine VA07A) and the second is taken from the IMSL library (ZXSSQ). Since the Jacobian has to be calculated numerically, the IMSL procedure performs better than the Fletcher one in terms of computer time. The difference between the two methods is more evident as the number of estimated parameters gets higher.

Even though the objective function and the numerical procedure selected gave excellent results in terms of computer time and numerical precision, some suggestions are given for improving the parameter estimation:

- use of generalized correlations (Cotterman *et al.*, 1986) for calculating the starting value of the parameters or taking the values for a similar hydrocarbon if the correlations are not applicable;
- adjustment of T^* with the objective function using vapor pressure data only;
- adjustment of T^* and V^* with the full objective function;
- adjustment of T^* , V^* and c with the full objective function (for systems without association);
- adjustment of T^* , V^* , c and Q with the full objective function (for associating substances).

DATA USED FOR CALCULATION

Nineteen substances have been selected and parameters have been estimated according to the procedure described above. Pseudo-experimental data generated using available correlations from the literature

have been used for McGarr Rackett liquid Spence (1986). ethane, pure h equation *et al.* (19 PVT data In Table is given from G

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have been considered. Wagner's equation has been used for vapor pressures, with parameters taken from McGarry (1983) or Smith and Srivastava (1986). Rackett's equation has been used to generate saturated liquid volumes, with parameters taken from Spencer and Adler (1978) or Smith and Srivastava (1986). For some compounds (nitrogen, methane, ethane, ethylene), PVT data above the critical temperature have been generated by very accurate virial equations of state with coefficients taken from Sychev *et al.* (1987). For the remaining ones high-temperature PVT data were obtained from the literature (Table 1).

In Table 1 information on substances and data sets is given. Values of quadrupole moments are taken from Gray and Gubbins (1984).

RESULTS

The results of the correlations are reported in Table 2 and Figs 1-3. Table 2 reports, for each compound investigated, the number of adjustable parameters, their optimum values and the average percentage deviations of liquid volumes and vapor pressures. In most cases the number of adjustable parameters is three, namely T^* , V^* and c . In some cases two (T^* and V^*) or four parameters (T^* , V^* , c and Q) are adjusted. Calculations have also been performed with

parameters from the generalized correlation (Cotterman *et al.*, 1986), restricted to the case of hydrocarbons.

The measure of the error is given by:

$$\% \text{ Avg. Abs. Dev.} = \frac{1}{k} \sum_i^k \left[\frac{|X^{\text{exp}} - X^{\text{calc}}|}{X^{\text{exp}}} \right] \quad (7)$$

where k is equal to n for saturation data and m for supercritical data; X stands for vapor pressure, saturated liquid volume or high temperature density.

Some of the selected substances have also been considered by Cotterman *et al.* (1986). For these substances parameters have been estimated using only saturation data at low temperature (cases indicated by LT in Table 2) and therefore the calculated supercritical data are extrapolated. The data prediction in the supercritical range is rather good. In the other cases, the best parameter values were obtained by regression of all the available data.

Correlation results for vapor pressure, saturated liquid volume and density are very good for substances not exhibiting association phenomena. For such substances deviations in vapor pressure and in saturated liquid volume are limited to 1% (Table 2). For benzene the influence of quadrupole moment as an adjustable parameter has been investigated. We

Table 1. Compounds investigated and experimental data used: saturation data (VLE) and supercritical data (PVT)

L.P.	Substance	Dipole moment (D) ¹	Quad. moment (B) ²	Number of data points		References for high temperature PVT data
				VLE	PVT	
1	Argon	—	—	20	50	Vargaftik, 1975
2	Nitrogen	—	—	20	50	Sychev <i>et al.</i> , 1987
3	Methane	—	—	20	50	Sychev <i>et al.</i> , 1987
4	Ethane	—	—	19	40	Sychev <i>et al.</i> , 1987
5	Propane	—	—	20	40	Vargaftik, 1975
6	Butane	—	—	18	35	Vargaftik, 1975
7	Pentane	—	—	35	—	—
8	Decane	—	—	20	—	—
9	Heptadecane	—	—	20	—	—
10	Ethylene	—	2.0	20	42	Sychev <i>et al.</i> , 1987
11	Benzene	—	3.6	13	25	Gehrig and Lentz, 1977
12	Toluene	—	0.0	20	—	—
13	Diphenyl	—	0.0	20	—	—
14	Naphthalene	—	0.0	10	—	—
15	Acetone	2.88	0.0	6	10	Keller and Stiel, 1977
16	Diethylketone	2.72	0.0	20	—	—
17	Methylchloride	1.9	1.23	18	48	Hsu and McKetta, 1964
18	Trifluoromethane	1.66	0.0	15	40	Sychev <i>et al.</i> , 1987
19	Ethylchloride	2.0	0.0	20	—	—
20	Ethylbromide	2.0	0.0	20	—	—
21	Carbon dioxide	—	3.9	20	60	Vargaftik, 1975
22	Hydrogen sulfide	0.97	1.0	15	48	Lewis, and Fredericks, 1968
23	Ammonia	1.47	1.15	20	60	Haar and Gallagher, 1978
24	Water	1.85	1.25	25	—	—
25	Methanol	1.7	1.20	26	—	—
26	Ethanol	1.44	1.90	25	—	—
27	Propanol	1.7	10.92	21	—	—
28	1-Decanol	2.0	0.0	20	—	—

¹Dipole moment in Debyes.

²Quadrupole moment in Buckingham.

Table 2. Results of correlations: saturation data (VLE) and supercritical data (PVT)[†]

Substance	Number of parameters	Optimal values of parameters				% Avg. absolute deviation		
		T^* (K)	V^* (cm ³ /mol)	C	Q (B)	Vapor press.	Liq. vol.	
							VLE	PVT
Argon	2	116.16	16.275	1.0	—	0.61	1.62	1.34
	3	119.04	16.653	0.94601	—	1.0	0.37	0.76
Nitrogen	LT	95.840	20.060	1.0	—	0.66	0.42	0.69
	2	95.817	20.051	1.0	—	0.71	0.38	0.69
	3	96.548	20.142	0.98433	—	0.53	0.53	0.65
Methane	LT	147.10	21.940	1.0	—	0.80	0.71	1.27
	2	147.34	21.703	1.0	—	0.86	0.58	1.16
	3	149.75	21.925	0.96794	—	0.89	0.59	0.78
Ethane	GC	204.17	30.282	1.4515	—	6.72	1.19	1.76
	2	224.79	30.507	1.2	—	1.85	1.85	0.89
	3	222.12	30.299	1.2281	—	0.75	2.04	0.91
Propane	LT	253.50	40.460	1.4470	—	0.39	1.18	1.95
	3	258.06	40.414	1.4014	—	1.35	2.10	1.19
Butane	GC	279.12	50.430	1.6488	—	1.41	1.18	2.25
	3	286.41	51.011	1.5610	—	1.62	0.82	1.36
Ethylene	2	205.71	27.662	1.2	—	0.77	0.44	1.27
	3	206.06	27.677	1.1962	—	0.91	0.47	1.24
Benzene	LT	368.10	51.610	1.6780	0.0 ¹	2.04	1.59	4.30
	LT	368.10	51.610	1.6780	3.6 ²	2.35	1.40	4.31
	3	373.88	51.007	1.6234	0.0 ¹	1.66	0.66	3.59
	3	374.75	51.162	1.6125	3.6 ²	1.49	0.61	3.51
	4	381.93	57.637	1.2020	11.64	0.20	0.77	2.48
Methyl chloride	3	296.40	31.627	0.99473	1.23 ³	1.24	1.68	2.05
	3	291.83	30.515	1.0575	0.0 ¹	1.45	1.62	1.43
Trifluoromethane ^a	4	199.45	31.223	1.0971	2.316	0.54	5.8	1.29
Trifluoromethane ^b	3 ⁴	199.65	27.931	1.2731	0.0 ¹	0.07	0.38	5.30
	3	196.70	29.354	1.3306	0.0 ¹	2.40	6.80	2.83
	0 ⁵	199.45	31.223	1.0971	2.316	0.23	6.35	4.00
Acetone	3	329.09	45.528	1.3861	0.0	0.66	3.04	0.94
Carbon dioxide	LT	200.80	21.090	1.2200	3.9	0.06	0.28	2.03
	3	205.04	21.206	1.1359	3.9 ⁶	0.60	1.78	1.23
Ammonia	LT	274.80	15.990	1.0510	1.15	0.38	2.66	2.25
	3	275.45	15.794	1.0264	1.15 ⁶	0.40	2.51	1.80
	3	279.15	15.188	1.1191	0.0 ¹	1.90	2.60	1.76
Hydrogen sulfide	LT	277.00	21.750	1.0970	1.0	0.24	0.24	2.39
	3	282.49	21.721	1.0517	1.0 ⁶	1.10	1.50	1.30
Water	LT	401.10	12.270	1.0520	1.25 ⁶	1.21	1.43	—
	3	401.24	12.254	1.0503	1.25 ⁶	0.97	1.36	—
Methanol	4	320.20	22.843	2.1607	1.190	2.53	0.66	—
Ethanol	4	290.14	30.248	3.0464	1.894	1.86	2.60	—
Propanol	4	284.94	42.546	2.5618	10.92	1.43	2.49	—

[†]LT = parameters from low temperature data, GC = parameters from correlation (Cotterman *et al.*, 1986). ^aVLE data from McGarry (1983) and PVT data from Spencer and Adler (1978). ^bVLE data from Smith and Srivastava (1986) and PVT data from Hou and Martin (1959). ¹Quadrupole moment not adjustable, set to 0.0. ²Quadrupole moment not adjustable, taken from Prausnitz *et al.* (1986). ³Quadrupole moment not adjustable, taken from Gray and Gubbins (1984). ⁴Objective function in terms of saturation data only. ⁵Parameters obtained from data reported in (a). ⁶Quadrupole moment not adjustable, taken from Cotterman *et al.* (1986).

reached the conclusion that the quadrupole moment should not be considered as an adjustable parameter unless strictly necessary, for example in the case of alcohols.

The parameters obtained (V^* , c , cT^*) were correlated with Bondi's volume (BV) as was suggested by Vimalchand *et al.* (1988) for a different equation. BV has been calculated according to the method de-

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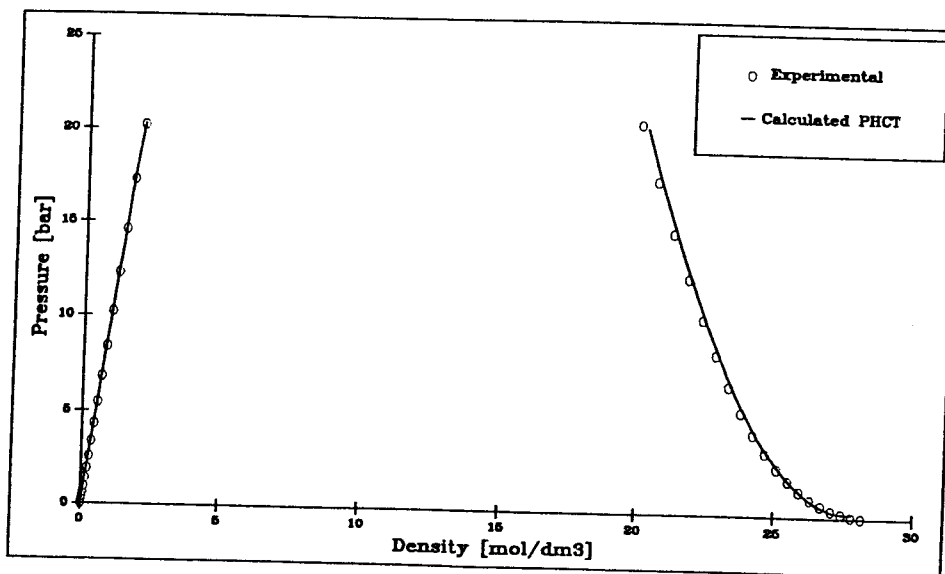


Fig. 1. Methane, low-temperature data (VLE).

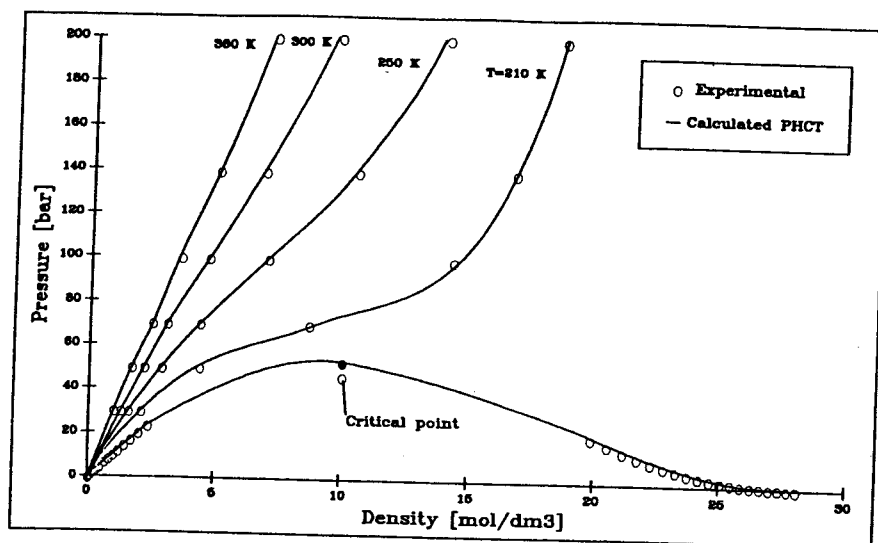


Fig. 2. Methane, high-temperature data (PVT) and critical zone: full lines are the PHCT calculated data.

scribed by Bondi (1968). In Figs 4-6 the plots of V^* vs BV , c vs BV and cT^* vs BV have been reported. The dependence of V^* on BV is linear for all types of substances. For c and cT^* the relation can be regarded as linear for non-hydrogen bonding substances.

The equation parameters (V^* , c and T^*) were predicted from Bondi's volume for some substances not included in the original data base and thereafter VLE and PVT data have been predicted. The results are reported in Table 3 labeled as "full prediction". It is interesting to point out that the equilibrium pressure is badly represented, but the volumetric property prediction is satisfactory. In order to improve phase equilibrium calculation, we derived T^* from

one single vapor pressure datum, still estimating V^* and c from the above mentioned correlations. The normal boiling temperature was used but any other vapor pressure datum may be used since the normal boiling point could be doubtful for high boiling substances. The results reported in Table 3 as "one point prediction" are rather good and surprisingly close to those obtained from the fitting of all the parameters to all the data points. Naturally the single point prediction is very sensitive to the goodness of the experimental data considered.

CONCLUSIONS

The Cotterman, Schwarz and Prausnitz equation of state gives very good results in the simultaneous

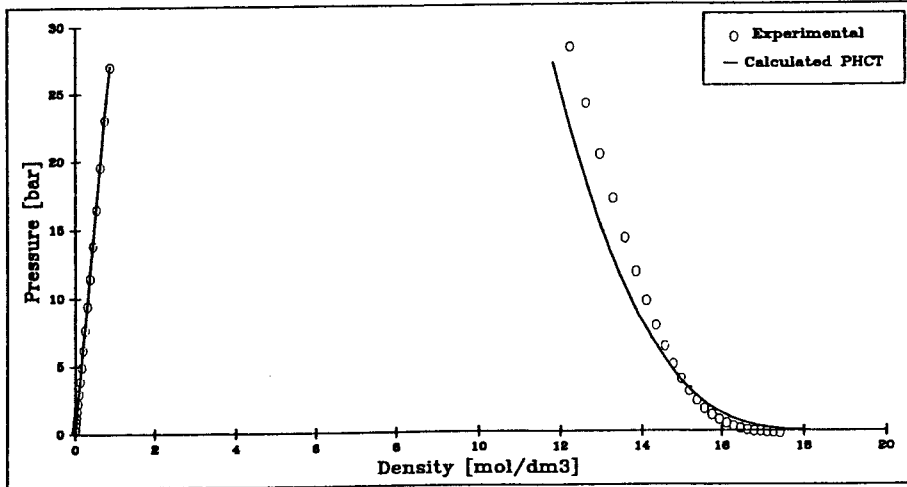


Fig. 3. Ethanol, low-temperature data (VLE).

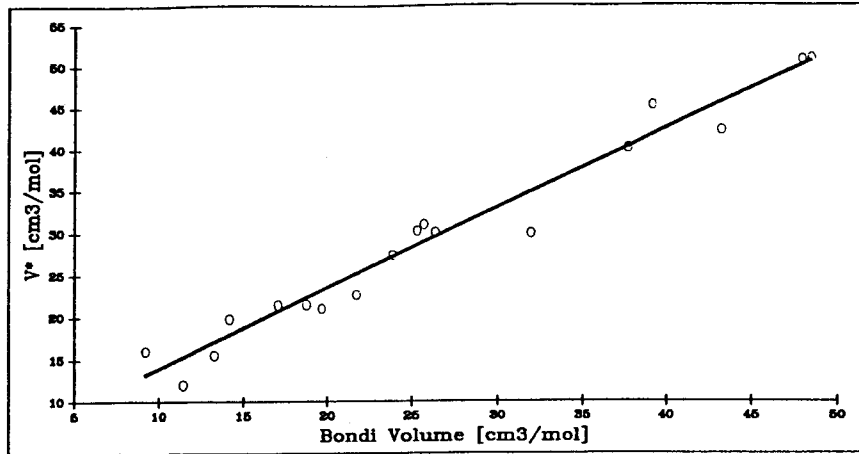


Fig. 4. Plot of volumetric parameter V^* vs Bondi's volume: the straight line represents the correlation proposed.

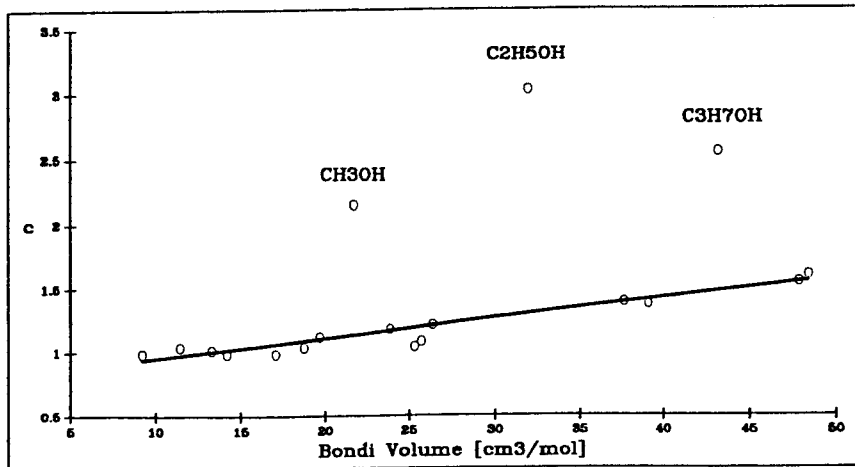


Fig. 5. Plot of parameter c vs Bondi's volume: the straight line represents the correlation proposed. Values for alcohols are shown.

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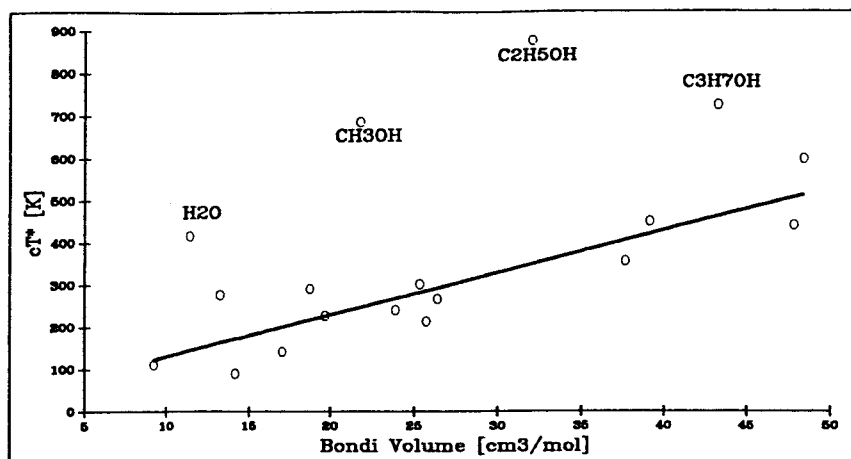


Fig. 6. Plot of parameter cT^* vs Bondi's volume: the straight line represents the correlation proposed. Values for alcohols and water are shown.

Table 3. Prediction

Substance	Full prediction (errors %AAD)			One point prediction (errors %AAD)			Parameters		
	Vapor press.	Liq. vol.		Vapor press.	Volume		T^* (K)	V^* (cm^3/mol)	C
		VLE	PVT		Sat. L	PVT			
Methane	89.3	15.4	33.8	3.66	4.37	2.35	143.62	20.668	1.0592
Ethane	51.2	8.89	10.2	0.86	4.96	1.25	225.02	29.573	1.2054
Propane	67.4	9.27	16.7	1.58	2.75	1.10	259.99	40.313	1.3817
Pentane	74.4	15.8	—	1.68	2.78	—	310.05	59.881	1.7030
Decane	87.2	18.4	—	1.87	3.21	—	368.52	108.800	2.5063
Heptadecane	—	—	—	1.79	4.87	—	402.83	177.29	3.6308
Toluene	96.4	4.99	—	2.21	2.71	—	389.95	61.297	1.7263
Diphenyl	243	8.27	—	1.71	1.38	—	472.66	92.064	2.2315
Naphthalene	554	9.36	—	0.19	3.09	—	470.91	75.738	1.9634
Ethylchloride	94.1	4.41	—	4.72	5.41	—	312.42	38.352	1.3496
Ethylbromide	246	0.88	—	3.58	4.49	—	342.31	41.011	1.3932
Diethylketone	8.49	1.94	—	2.29	2.24	—	365.84	61.287	1.7261
1-Decanol	68.1	7.37	—	17.4	2.05	—	413.62	113.20	2.5785

correlations of VLE and PVT data for the compounds investigated. Physically meaningful parameters are obtained for the compounds listed in Table 2, thus allowing a generalized simple correlation in terms of Bondi's volumes to be established. The calculations are at least as good as those obtained with other equations of state, but this model avoids the use of the critical coordinates, which are difficult to estimate and retrieve especially for compounds interesting in SFE processes.

For the substances considered it is possible to predict supercritical density data from saturation data with an accuracy which can be regarded as sufficient for chemical engineering process design. The representation of vapor pressures and saturated liquid and vapor volumes is as good as that of the density at supercritical temperature.

Alcohol saturation data are correlated only if the quadrupole moment is considered as an adjustable

parameter: in this case the error of correlation is comparable to that of the other substances. Equation parameters for water and alcohols do not follow the generalized correlation and their physical significance is doubtful. This is essentially due to hydrogen bonding phenomena that this equation does not account specifically for. On the other hand, for some hydrogen bonding substances, like ammonia and hydrogen sulfide, the correlations give good results with physical significance of the equation parameters.

The generalized linear correlations for all the parameters cT^* , V^* and c with Bondi's volume do not give satisfactory results for saturation data. We suggest the use of the generalized correlations for the V^* and c parameters and a single vapor pressure datum for the estimation of the T^* parameter (the only adjustable parameter left): good results are obtained for non-hydrogen bonding components.

Finally, we should stress that the PHCT equation

Table 4. Comparison among calculated and experimental critical coordinates

Substance	T_c^{exp}	T_c^{calc}	P_c^{exp}	P_c^{calc}	V_c^{exp}	V_c^{calc}
Methane	190.4	196.2	46.8	53.2	99.2	99.8
Water	647.3	702.5	221.2	357.8	57.1	52.0
Carbon dioxide	304.1	313.5	73.8	93.0	93.9	90.6
Ethane	305.4	315.1	48.4	56.9	148.3	149.2
Acetone	508.1	548.6	47.0	72.4	209.0	216.0
Propane	369.8	381.5	42.5	49.3	203.0	204.1
Benzene	562.2	569.3	48.9	52.7	259.0	281.0
n-Octane	568.8	574.1	24.9	26.0	492.0	535.0
n-Decane	617.7	630.1	21.2	22.9	603.0	595.0

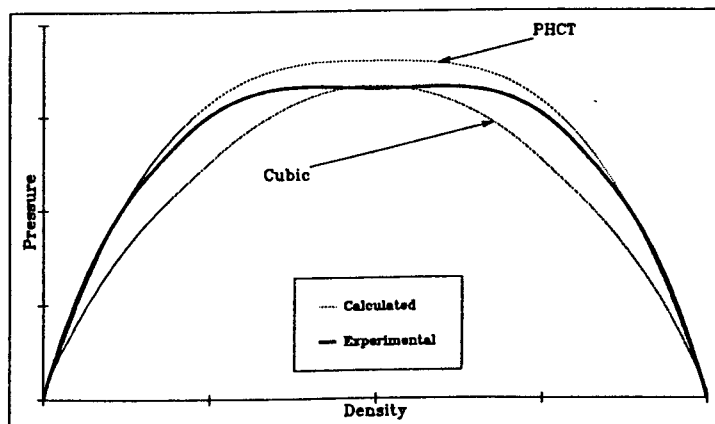


Fig. 7. Qualitative behavior in the critical region for the PHCT equation in comparison with a cubic equation (full line is the experimental data).

of state gives very good representations of both the supercritical and subcritical regions, but fails in the vicinity of the critical point. The calculated critical point is systematically shifted to higher pressure and temperature as can be clearly seen in Fig. 2, where a false phase split above the experimental critical point is predicted. Table 4 reports, for some selected compounds, the difference between the calculated and experimental critical coordinates. Large deviations are seen in T_c and P_c , especially for polar substances. The calculated critical compressibility factors (not reported) are too large (see also Beret and Prausnitz, 1975) although they decrease with increasing c , in agreement with experiment. The critical volume is correctly predicted. The calculated critical point is located on the prolongation of the Clausius–Clapeyron curve beyond the experimental critical point because the representation of the vapor pressure curve is good. Therefore large errors in T_c generate large errors in P_c . This is evident with polar substances, where the physical meaning of the adjustable parameters is doubtful. Similar problems also arise with cubic equations of state, but in terms of volumes. Better results in the critical region are obtained by fitting the parameters to PVT data with reduced temperature close to one, but the results at high and low pressure are poor. Figure 7 shows the qualitative

behavior of the PHCT equation in comparison to a cubic equation. The translation parameter, normally applied to cubic equations, only has the effect of shifting the curve to the right to refine the liquid density predictions, but such improvement is at the expense of a worse vapor volume prediction. Advantages and limitations of the different types of equations are clearly seen.

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NOTATION

a	Helmholtz function
BV	Bondi volume
c	no. of external degrees of freedom
k	Boltzmann's constant
N_{av}	Avogadro's number
P	pressure
Q	quadrupole moment
q	surface area of the molecules
R	gas constant
r	no. of segments
T	temperature
V	volume

- v^* soft core molar volume
- Z compressibility factor
- Greek characters**
- μ dipole moment
- σ soft core diameter of one segment
- ϕ fugacity coefficients
- ϵ potential energy per unit surface area

Superscripts and subscripts

- c critical condition
- calc calculated
- exp experimental
- L liquid phase
- pert perturbation or attractive term
- r residual
- ref reference or repulsive term
- V vapor phase

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APPENDIX A. EQUILIBRIUM CALCULATION PROCEDURE

The solution of eq. (5) is based on Newton's method, taking advantage of the following thermodynamic condition:

$$\frac{\delta \ln \phi}{\delta P} = \frac{Z - 1}{P} \quad (A1)$$

The pressure derivatives of $\ln \phi$ are available. The iterative procedure is written in terms of $\ln P$ because it is computationally faster. Accordingly the iterative formula is then:

$$\ln P_{j+1} = \ln P_j - \frac{\ln(\phi^V / \phi^L)_j}{(Z^V - Z^L)_j} \quad (A2)$$

APPENDIX B. OBJECTIVE FUNCTION

Normally, the objective function used for parameter estimation is the following:

$$OF = \sum_i^n \left[\frac{(P^{\text{exp}} - P^{\text{calc}})}{P^{\text{exp}}} \right]^2 + \sum_i^n \left[\frac{(V_L^{\text{exp}} - V_L^{\text{calc}})}{V_L^{\text{exp}}} \right]^2 + \sum_j^m \left[\frac{(V^{\text{exp}} - V^{\text{calc}})}{V^{\text{exp}}} \right]^2 \quad (B1)$$

where P is the saturated pressure, V_L is the saturated liquid volume, V is the fluid volume for PVT data, n is the number of VLE data points ($T < T_c$) and m is the number of PVT data points. For each objective function evaluation, the equilibrium pressure (P^{calc}) for all n data points must be calculated. Consequently the CPU time for a complete parameter estimation can be very high, especially for a system with a bad initial estimate of the parameters. In order to reduce the calculation time, the first part on the right hand side of eq. (B1) has been modified. It can be proved that the new objective function reduces to eq. (B1) if some assumptions are made. In eq. (5) we have:

$$F(P^{\text{calc}}) \equiv 0 \quad (B2)$$

where P^{calc} is a calculated equilibrium vapor pressure. For small values of $(P - P^{\text{calc}})$ one can expand the function $F(P)$ around the point P^{calc} into a Taylor series cut after the second term and take into account the condition (B2). So one

gets:

$$F(P) \approx \frac{\delta F}{\delta P} (P - P^{\text{calc}}). \quad (\text{B3})$$

The value of the pressure derivative of F is estimated from eq. (A1):

$$\frac{\delta F}{\delta P} = \frac{V_L - V_V}{R T^{\text{exp}}} \quad (\text{B4})$$

where V_L and V_V are the saturated liquid and vapor volumes at T^{exp} and P^{calc} respectively. Far from the critical point one can assume that:

$$V_V \gg V_L \quad (\text{B5})$$

and that the vapor phase is ideal. If we assume $P \approx P^{\text{calc}}$, which is reasonable in the vicinity of the minimum of the objective function, the following equation holds:

$$\frac{\delta F}{\delta P} = -\frac{1}{P} \quad (\text{B6})$$

and the following relationship is obtained:

$$F(P) \approx -\frac{P - P^{\text{calc}}}{P} \quad (\text{B7})$$

or

$$[\ln \phi^V(P) - \ln \phi^L(P)]^2 \approx [(P - P^{\text{calc}})/P]^2. \quad (\text{B8})$$

Substituting $P = P^{\text{exp}}$ the objective function becomes:

$$\begin{aligned} OF = & \sum_i^n [\ln \phi^V(P^{\text{exp}}) [-\ln \phi^L(P^{\text{exp}})]^2 \\ & + \sum_i^n \left[\frac{(V_L^{\text{exp}} - V_L^{\text{calc}})}{V_L^{\text{exp}}} \right]^2 \\ & + \sum_j^m \left[\frac{(V_V^{\text{exp}} - V_V^{\text{calc}})}{V_V^{\text{exp}}} \right]^2. \end{aligned} \quad (\text{B9})$$

The objective function, eq. (B9), can be used in the first step of the optimization procedure. Then one has two possibilities: to consider the values of parameters obtained in the initial step as the best ones, or to consider these values as an initial estimate for a new optimization with the objective function [eq. (B1)]. Both methods have been investigated and it was found that the results are essentially the same, apart from the fact that the first method takes much less computer time.