Phase-Equilibria Calculation by Group-Contribution Perturbed-Hard-Sphere-Chain Equation of State

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A group-contribution (GC) method was coupled with the perturbed-hard-sphere-chain (PHSC) equation of state (EOS) to predict its characteristic parameters. This model can describe both equilibrium and volumetric properties of regular fluids and chain-like molecules. The estimation of group contributions for the characteristic volume, surface area, and interaction energy was based only on vapor-pressure and saturated liquid-density values of low-molecular-weight compounds. It was successful in estimating the EOS parameters of high-molecular-weight compounds and chain-like molecules. Some application results show its reliability but the method was not applied to all classes of compounds. Good estimation of polymer density was obtained by GC PHSC with only the knowledge of their molecular structure. For mixtures, the original model was retained; binary interaction parameters were regressed from vapor−liquid equilibria of binary systems. In most cases, only one binary interaction parameter is enough to describe binary systems in a wide range of temperatures. The same model is extended to the calculation of liquid−liquid equilibria of a system exhibiting both upper critical solution temperature (UCST) and lower critical solution temperature (LCST). In summary, the data required for calculating multicomponent phase equilibria are the molecular structure in term of functional groups and binary interaction parameter values.

Introduction and Background

Phase-equilibrium calculations are essential in the design and operation of chemical processes. Specifically, it is of paramount importance to be able to calculate all the relevant fundamental properties of the substances of interest in all the required process conditions. Unfortunately, in many cases, only the chemical structure is well known, and no relevant experimental information is available to fine-tune semiempirical models. As a consequence, the problem of estimating reasonable and physically consistent equation-of-state (EOS) parameters for pure fluids plays a fundamental role, especially when the model is used within a process simulator.

There are many applications where the estimation of pure properties are important. One such field is polymer solution, but other cases, where long-chain molecules are involved, such as lubricant oils employed in the refrigeration field or heavy crude oil in petroleum fractionation, are also important. In all these cases, classic molecular theories are not applicable, and one should resort to a theory that takes into account asymmetrical large molecules. Many models are available, but only a few of them are suitable to calculate thermodynamic properties and phase equilibria in systems where the properties of pure compounds are not known.

This is typically a problem with all EOSs based on molecular parameters that have to be determined from the fitting of experimental data. Traditionally, cubic EOSs use molecular

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constants such as critical conditions and vapor pressure to scale the parameters, which are often not available or are questionable. Polymers are a typical case where, at most, chemical formulas and molecular weights are known.

In the last decade some alternative solutions have been proposed. For example, polymer parameters were regressed from experimental pure polymer PVT data at different pressures. Song et al. (1996) pointed out that, even if the energy interaction parameter of an EOS is almost insensitive to density data, PVT data spread over a wide range of pressures could fairly characterize the energy interaction. In that work the perturbed-hard-sphere-chain (PHSC) EOS was used. An analogous procedure was followed in the case of other off-lattice models; in the statistical-association-fluid-theory (SAFT) equations, Huang and Radosz (1990, 1991) proposed some modifications in which a recipe to estimate only the volume parameter was provided. Acceptable results were shown only for the alkane homologous series, and no solution was suggested for the energy parameter of the SAFT EOS.

A more general approach was proposed by High and Danner in 1989. These authors developed a group-contribution lattice-fluid (GCLF) EOS for polymer solutions. A number of modifications followed the original article (High and Danner, 1990; Lee and Danner, 1996a,b). These modifications have been reliably applied to the prediction of the vapor–liquid equilibria (VLE) of polymer-solvent systems.

The GCLF EOS works well, but when written in terms of molecular species, it is still a lattice theory with all the limitations of such a theory. On the other hand, off-lattice theories based on freely jointed tangent hard spheres can better describe the physics of real polymer systems, as shown by Song et al. (1994a,b).

Another method for determining the EOS parameters of physically based models was recently proposed by Fermeglia and Pricl (1999a,b), who determined the parameters for pure polymers by coupling molecular mechanics and molecular dynamics techniques with an EOS theory. In particular, the characteristic volume, surface area, and energy parameters were calculated for the PHSC and the lattice-fluid EOS. The authors showed good results in the prediction of pure-component properties; the determination of molecular EOS parameters by computer simulation seems to be of general applicability, but still needs some refinement and, in terms of usage of computer resources, to extend the technique to extreme conditions.

In this work, a new method, complementary to the previous one but based on the more classic idea of group contributions similar to that of High and Danner (1990), has been derived for estimating parameters of a physically based EOS. The characterization of the parameters is achieved by using experimental PVT and VLE data of low-molecular-weight compounds. The selected EOS model is the PHSC theory; since this equation is characterized by an accurate physical reference model, it can describe both volumetric and equilibrium properties with good accuracy. With respect to other EOSs (such as SAFT), derived from the analogous theory, the PHSC EOS ensures similar performances even if this EOS is slightly simpler. In a previous work of Bertucco et al. (1999) both the VLE and liquid–liquid equilibria (LLE) of binary mixtures of lubricant oils and refrigerant were evaluated using a preliminary development of the GC PHSC. In this work, we extend the method to a larger class of compounds. Pure property and mixture calculations of VLE and LLE are performed in order to check the reliability and accuracy of the proposed technique.

PHSC EOS Model

The PHSC EOS considered here was developed by Song et al. (1994a,b) using the expression for hard-sphere chains as the reference term (Chiew, 1990) and a van der Waals attractive form for the perturbation

$$\left(\frac{P}{\rho kT}\right) = 1 + r^2 b\rho g(d^+) - (r-1)[g(d^+)-1] - \frac{r^2 a\rho}{kT} \quad (1)$$

where P is the pressure; T the absolute temperature; $\rho = N/V$ the number density; N the number of molecules; V the volume of the system; k the Boltzmann's constant; d the hard-sphere diameter; and $g(d^+)$ the pair radial distribution function of hard spheres at contact. Three segment-based parameters appear in Eq. 1: r is the number of segments per molecule; a reflects the attractive forces between two nonbonded segments; and b is the van der Waals segment covolume. In Eq. 1 only the reference term accounts for chain connectivity.

Because the effective hard-sphere diameter and attractive energy parameters are theoretically-based functions of temperature, the expressions for a and b are obtained by applying the method of Song and Mason (1989)

$$a(T) = \frac{2\pi}{3}\sigma^3 \epsilon F_a(kT/\epsilon) \quad (2)$$

$$b(T) = \frac{2\pi}{3}\sigma^3 F_b(kT/\epsilon) \quad (3)$$

where ϵ is the depth of the minimum in the pair potential, and σ is the separation distance between segment centers at this minimum; and F_a and F_b are universal functions of the reduced temperature kT/ϵ. Song et al. (1996) determined an empirical approximation of these functions from the thermodynamic properties of spherical molecules such as argon and methane ($r = 1$) over wide ranges of temperature and density. The dependence of F_a and F_b on the number of segments r has been neglected.

The PHSC EOS for simple fluids and spherical molecules contains two parameters: σ and ϵ/k. When applied to chainlike molecules, a third parameter (r) is needed. It is convenient to redefine these parameters through a characteristic volume, V^*, a characteristic surface area, A^*, and a characteristic ⟨⟨cohesive⟩⟩ energy, E^*, per mole of molecules

$$V^* = (\pi/6) r\sigma^3 N_A \quad (4)$$

$$A^* = \pi r \sigma^2 N_A \quad (5)$$

$$E^* = r(\epsilon/k) R_g = r\epsilon N_A \quad (6)$$

where N_A and R_g are the Avogadro's number and the universal gas constants, respectively. These pure-component parameters are physically significant quantities that reflect the size, shape, and interaction energy of the molecules.

Extension of the PHSC EOS to mixtures is obtained by applying the one-fluid-mixing rules to the EOS parameters, which leads to the following equation (Song et al. 1994a)

$$\frac{P}{\rho kT} = 1 + \rho \sum_{ij}^{m} x_i x_j r_i r_j b_{ij} g_{ij}\left(d_{ij}^{+}\right) - \sum_{i}^{m} x_i (r_i - 1)\left[g_{ii}\left(d_{ii}^{+}\right) - 1\right] - \frac{\rho}{kT} \sum_{ij}^{m} x_i x_j r_i r_j a_{ij} \qquad (7)$$

where $x_i = N_i/N$ is the number fraction of molecules of species i, r_i is the number of segments for the ith component, and $g_{ij}(d_{ij}^{+})$ is the i, j pair radial-distribution function of hard-sphere mixtures at contact.

The exact statistical mechanical expression for $g_{ij}(d_{ij}^{+})$ is given by Boublik (1970) and Mansoori et al. (1971)

$$g_{ij}(\eta, \xi_{ij}) = \frac{1}{1-\eta} + \frac{3}{2}\frac{\xi_{ij}}{(1-\eta)^2} + \frac{1}{2}\frac{\xi_{ij}^2}{(1-\eta)} \qquad (8)$$

where η is the packing fraction

$$\eta = \frac{\rho}{4} \sum_{i}^{m} x_i r_i b_i \qquad (9)$$

and ξ_{ij} is expressed by

$$\xi_{ij} = \left(\frac{b_i b_j}{b_{ij}}\right)^{1/3} \frac{\rho}{4} \sum_{k}^{m} x_k r_k b_k^{1/3} \qquad (10)$$

For pure components, ξ_{ij} becomes equal to η, while Eq. 8 gives the Carnahan–Starling EOS for hard spheres when $r = 1$.

The two parameters for each pair of components (a_{ij} and b_{ij}) are obtained by extensions of Eqs. 2 and 3

$$a_{ij} = (2\pi/3)\sigma_{ij}^3 \epsilon_{ij} F_a\left(kT/\epsilon_{ij}\right) \qquad (11)$$

$$b_{ij} = (2\pi/3)\sigma_{ij}^3 F_b\left(kT/\epsilon_{ij}\right) \qquad (12)$$

where F_a and F_b are the same universal functions as the pure component (Song et al., 1996).

The combining rules for σ_{ij} and ϵ_{ij} are defined by

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)(1 - \lambda_{ij}) \qquad (13)$$

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}\,(1 - k_{ij}) \qquad (14)$$

Two binary segment–segment interaction parameters, k_{ij} and λ_{ij}, are introduced in the combining rule for the parameters ϵ and σ.

In this work the values for k_{ij} are regressed from experimental binary VLE data. The λ_{ij} interaction parameter is not used, since an accurate correlation by GC-PHSC has been obtained discharging all theory approximations in the energy-adjustable parameter, k_{ij}.

For equilibrium calculations, even though the expressions reported earlier are in terms of pressure, the EOS, like all other models developed in the framework of a statistical mechanics background, is developed in terms of a residual Helmholtz function. In this way, once the EOS is established, other thermodynamic functions, such as enthalpy, entropy, and chemical potential, can be obtained by partial differentiation of the residual reduced Helmholtz function with respect to temperature, volume, and number of mols. To make the mathematical derivation easier, Eq. 7 has been modified from the molecule-number basis to the segment-number basis. The segment basis independent variables are temperature T, segment density $\rho_r = N_r/V$, and segment fraction $\phi_i = N_i r_i/N_r$, where N_r is the total number of segments in the system

$$N_r = \sum_{i}^{m} N_i r_i \qquad (15)$$

The relation between x_i and ϕ_i is

$$x_i = \frac{(\phi_i/r_i)}{\sum_{j}^{m} (\phi_j/r_j)} \qquad \phi_i = \frac{x_i r_i}{\sum_{j}^{m} x_j r_j} \qquad (16)$$

In terms of T, ρ, and ϕ_i Eq. 7 can be written as

$$\frac{P}{\rho_r kT} = 1 + \rho_r \sum_{ij}^{m} \phi_i \phi_j b_{ij} g_{ij}\left(d_{ij}^{+}\right) - \sum_{i}^{m} \phi_i \left(1 - \frac{1}{r_i}\right) g_{ii}\left(d_{ii}^{+}\right) - \frac{\rho_r}{kT} \sum_{ij}^{m} \phi_i \phi_j a_{ij} \qquad (17)$$

The general equation for calculating the Helmholtz energy from a pressure-explicit EOS is (Prausnitz et al., 1986)

$$A(T,V,N_i) = \sum_{i}^{m} A_i^0(T) + \int_{V}^{\infty} \left(P - \frac{NkT}{V}\right) dV + kT \sum_{i}^{m} N_i \ \ln\left(\frac{N_i kT}{V}\right) \qquad (18)$$

The integration of Eq. 18 and the differentiation of the Helmholtz energy

$$\mu_k = \left(\frac{\partial A}{\partial N_k}\right)_{T,V,N_{i \neq k}} \qquad (19)$$

gives the chemical potential of component k in the mixture

$$\frac{\mu_k}{kT} = \frac{\mu_k^0}{kT} + 2r_k\,\rho_r \sum_{i=1}^{m} \phi_i b_{ik} W_{ik} + \sum_{ij=1}^{m} \phi_i \phi_j b_{ij} \left(N_r \frac{\partial W_{ij}}{\partial N_k} \right) \quad (20)$$

$$-(r_k - 1)Q_{kk} - \sum_{i=1}^{m} \phi_i \left(1 - \frac{1}{r_i}\right) \left(N_r \frac{\partial Q_{ii}}{\partial N_k} \right) \quad (21)$$

$$-\frac{2r_k\,\rho_r}{kT} \sum_{i=1}^{m} \phi_i a_{ik} + \ln\left(\frac{\phi_k}{r_k} \rho_k kT \right) \quad (22)$$

The expressions for W and Q are the same as those reported in the work of Song et al. (1994a). The thermodynamic functions just derived have been used for VLE and LLE calculations in this work.

Parameter Determination Procedure

The estimation of group contributions for the characteristic volume, V^*, the characteristic surface area, A^*, and the characteristic ⟨⟨cohesive⟩⟩ energy, E^*, was carried out in two steps: (1) the regression of the values of the pure molecular parameters V^*, A^*, and E^* for each low-molecular-weight compound, and (2) the assignment and evaluation of group contributions.

In the first step, the characteristic parameters were obtained by fitting both vapor pressure and saturated liquid densities above 1 bar (or PVT data at 1 bar when the temperature is under the normal boiling point).

For the volatile, that is, low molecular weight, fluids, vapor pressures are normally available so that both the PVT and equilibrium data can be used for evaluating the pure-component parameters. The procedure of the regression used in this work was the same as in Song et al. (1994b, 1996), and both liquid–density and vapor–pressure data were used to fit the pure-component parameters.

In the case of high-molecular-weight components, since vapor pressures are not known, their parameters cannot be determined in the same way as for volatile fluids. To overcome this difficulty, Song et al. (1994b, 1996) proposed a method for determining the parameters of high-molecular-weight components: this method requires the knowledge of PVT data at different pressures, which are not always easily available. This method is based on the limit of the EOS when the number of chain segments becomes infinite. For $r \to \infty$, Eq. 1 can be written as

$$\left(\frac{p}{\rho_r kT} \right) = 1 + b\rho_r g(d^+) - g(d^+) - \frac{a\rho_r}{kT} \quad (23)$$

with $\rho_r = r\rho$. This approximation is reasonable for many applications, provided the molecular weight of the polymer is above 1,000 Da (Song et al., 1994b, 1996). In order to overcome such limitations, in this work we refer to Eq. 1.

In the pure-component-parameter determination procedure developed, only experimental data of low-molecular-weight substances (within the 5% experimental uncertainty for vapor pressure and 3% for density) were used for regression purposes, in order to have an appropriate and reliable data-base. Many compounds with different functionalities were included in the data-regression procedure, such as alkanes, branched alkanes, alkenes, alkines, aromatics, cycloalkanes, esters, ethers, ketones, aldehydes, fluorinated, and chlorinated compounds. The vapor pressure, saturated liquid density, and PVT experimental data used in the regression were selected from Daubert and Danner (extant 1994).

The regressions were performed in the temperature range between 300 and 400 K, which is far enough from the triple and critical points of all compounds included in the parameter-estimation procedure. In this way distortions due to particular phenomena, such as fluctuations at the critical condition, were avoided. Moreover, this temperature range includes the vast majority of industrial process conditions.

The minimized objective function is a combination of two contributions

$$\text{obf} = \frac{1}{N_P} \sum_{i=1}^{N_P} \left(\frac{\rho_{\text{calc}} - \rho_{\text{exp}}}{\rho_{\text{exp}}} \right)^2 + \left(\frac{P_{\text{calc}} - P_{\text{exp}}}{P_{\text{exp}}} \right)^2 \quad (24)$$

where ρ_{exp} and ρ_{calc} are, respectively, the experimental and calculated saturated liquid density of a pure compound, and P_{exp} and P_{calc} the experimental and calculated vapor pressure, respectively.

The values obtained were examined thoroughly and a linear relationship between them and their molecular properties was found. This relationship formed the basis for deriving the present group-contribution method. The main result is that parameters V^*, A^*, and E^* are directly proportional to the number of carbon atoms for the series of normal alkanes (Figure 1a, 1b, and 1c). According to Figure 1c, the linearity also holds for parameter E^*, even though the data scattering is more pronounced in this case.

No temperature dependency was included in the energetic parameter. In a similar model (GCLF EOS by High and Danner, 1989) the number of temperature-dependent energetic parameters was two or three (Lee and Danner, 1996a,b).

As the second step, the GC values were determined from the molecular parameters previously obtained. The subdivision of main group and subgroups is reported in Table 1; it was derived from those developed by Hansen et al. (1991), for UNIFAC with suitable modifications.

The pure-component parameters can be calculated by

$$V_i^* = \sum_{k=1}^{n} \upsilon_k V_k^* \quad (25)$$

$$A_i^* = \sum_{k=1}^{n} \upsilon_k A_k^* \quad (26)$$

$$E_i^* = \sum_{k=1}^{n} \upsilon_k E_k^* \quad (27)$$

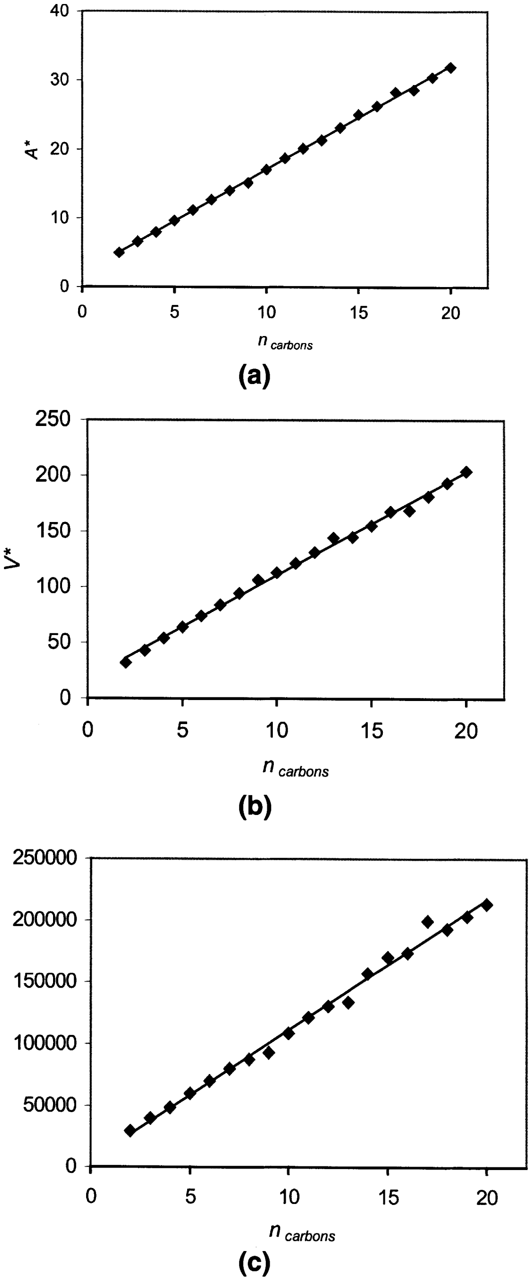
where the specific parameter contribution for each group, k, has index k, and υ_k is the number of groups, k, in the compound i considered.

The group parameters A_k^*, V_k^*, and E_k^* were independently determined by a linear regression using Eqs. 25–27. An indication of the error [absolute deviation (AD)] in the prediction of density and vapor pressure is reported for normal alkanes in Table 2: the uncertainty in density estimation is as low as 2% for almost all alkanes, while that in the vapor pressure is very sensitive to the energetic parameters, so the error is larger but often within 10%. For these reasons, the estimation of pure parameters by group contributions is suggested only if the properties of the fluid are not available; otherwise they are better fitted on PVT and VLE data.

The first step was to determine group contributions corresponding to a family of compounds whose experimental data showed the lowest uncertainties. Other families with higher uncertainties were considered at a later stage of the model development. The values of all groups considered are shown in Table 1.

Table 1. Values of the Group-Contribution Parameters.

Main Groups	Groups	A^*_{GC} (10^8 cm^2/mol)	V^*_{GC} (cm^3/mol)	E^*_{GC} (bar cm^3/mol)
CH_n	CH_3	21.541	14.227	16,040.0
	CH_2	16.34	11.296	9,414.0
	CH	8.228	8.241	− 1,106.0
	C	0.00	5.478	− 13,027.0
C = C	$CH_2 = CH$	34.098	21.589	23,005.0
	CH = CH	26.895	20.796	13,542.5
	$CH_2 = C$	25.421	17.695	13,467.6
	CH = C	23.902	15.040	11,225.7
	C = C	17.936	11.785	5,390.0
C ≡ C	C ≡ C	24.103	17.626	18,739.0
	HC ≡ C	28.311	20.060	22,915.3
ArCH	ACH	13.737	9.216	11,281.7
	AC	5.280	6.319	1,079.4
Cycle	$cyCH_2$	15.625	10.930	10,999.7
	cyCH	5.090	9.423	− 1,969.0
	cyCH = CH	25.591	19.440	19,555.0
Ether	—O—	16.429	2.618	16,303.7
Esther	COO	36.519	15.134	37,243.8
Ketons	C = O	25.540	12.536	26,535.7
Aldeid	CHO	34.550	13.067	41,915.3
Fluoro	F	12.684	5.548	11,773.2
Chloro	Cl	19.595	13.050	19,493.8
Amine	NH_2	31.713	13.969	43,537.4
CO_2		4.182	16.351	42,955.0



(a)

(b)

(c)

Figure 1. Characteristic parameter, (a) A^*, (b) V^*, and (c) E^* vs. number of carbon atoms for the series of normal alkanes.

Prediction of Pure-Component Properties

On the basis of Table 1, it is possible to extrapolate the pure parameters of the PHSC EOS to heavy-molecular-weight compounds such as polymers. The only input required for the model is the structure in terms of functional groups and the molecular weight.

Table 3 reports density predictions for a selection of common polymers and other compounds. The molecular weight of the polymer is often quite dispersed, but this approximation is not taken into account, so a number-average molecular weight was used. The method currently proposed is able to reproduce the experimental density in a wide range of temperatures and pressures with an average error of 5% at worst. This semiquantitative result is due to the strong extrapolation; anyway, the proposed method is interesting, as only the knowledge of the molecular structure is required.

The results reported show clearly that the group-contribution method works better for relatively large molecules, ensuring good prediction of both equilibrium and volumetric properties. In Figures 2 and 3 predictions of the liquid density of a lubricant oil (POE with a molecular weight of 700) and a vapor pressure of *n*-C36 are reported.

In the particular case of a lubricant oil, the error is less than 2% in a wide range of temperatures, as shown in Table 3. An erroneous behavior is found in the density prediction of all systems analyzed, and it increases with the molecular weight: the temperature dependence of the calculated density curve is higher than the expected one. This is probably due to the approximation of the temperature-dependence

Table 2. Statistical Errors for the Regression of Pure Parameter vs. Prediction by a Group-Contribution Method in the Case of Normal Alkanes

Compound	$AD(\Delta\rho/\rho\%)_{\mathrm{reg}}$	$AD(\Delta p/p\%)_{\mathrm{reg}}$	$AD(\Delta\rho/\rho\%)_{GC}$	$AD(\Delta p/p\%)_{GC}$
C5	2.28	0.707	6.37	29.8
C6	1.92	0.703	3.96	25.7
C7	1.89	0.825	2.65	22.1
C8	1.76	0.777	2.14	18.2
C9	1.71	0.710	1.82	14.6
C10	1.55	0.725	1.64	9.84
C11	1.62	0.550	1.55	5.46
C12	1.56	0.535	1.51	1.68
C13	1.41	0.642	1.37	3.43
C14	1.44	0.661	1.46	7.03
C15	1.31	0.790	1.47	8.03
C16	1.43	0.611	1.48	14.4
C17	1.38	0.688	1.51	19.8
C18	1.35	0.779	1.57	19.3

Table 3. Statistical Parameters of Prediction of a POE Lubricant Oil and Polymers: High Density Polyethylene (HPDE), *iso*-poly1-Butene (*i*-PB), Polyisobutylene (PIB), and Polystyrene (PS)

Compound	T[K]	P [bar]	N_P	AD ($\Delta\rho/\rho\%$)	Ref.
POE	253–343	1	19	0.96	*
HDPE	472–415	1–2,000	67	3.90	**
i-PB	406–514	1–1,960	45	5.06	†
PIB	325–383	1–1,000	55	4.68	††
PS	388–468	1–2,000	69	2.43	‡

*Martz et al. (1994).
**Olabisi and Simha (1975).
†Zoller (1979).
††Beret and Prausnitz (1975).
‡Quach and Simba (1971).

functions, F_a and F_b, of the energetic parameter, which are required to be insensitive to the number of segments.

Anyway, the purpose of this work is not to accurately reproduce experimental properties such as density, but to develop a method for providing a set of physically consistent PHSC EOS pure parameters for high-molecular-weight compounds, which are necessary for multicomponent phase-equilibria calculations. Nevertheless, the accuracy of the prediction of the pure properties can be considered acceptable; furthermore, the method is able to increase the accuracy and the physical effect of the VLE and LLE calculations.

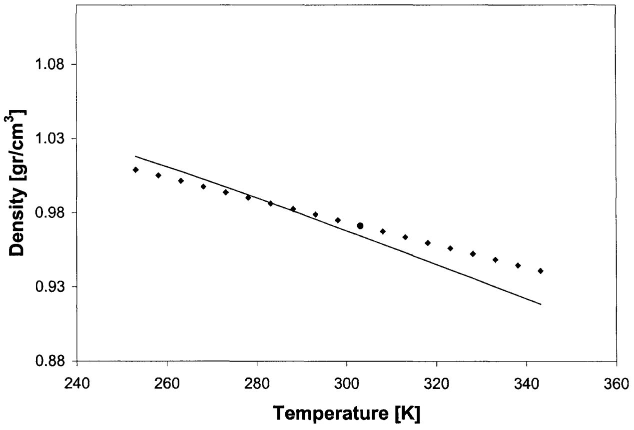


Figure 2. Prediction for POE lubricant oil liquid density.

Data from Martz et al. (1994).

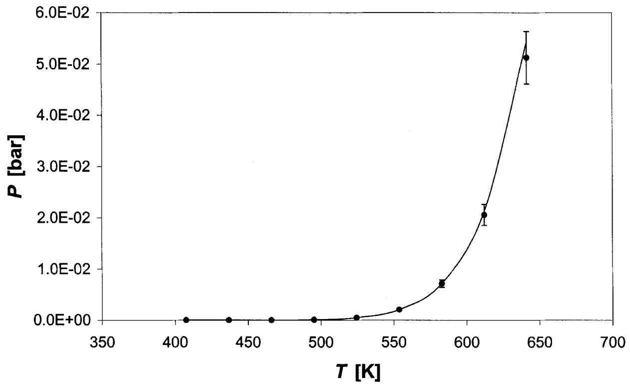


Figure 3. Prediction for nC36 of saturated liquid density.

Data from Daubert and Danner, (1993).

Vapor–Liquid Equilibria

The VLE calculations were performed for some binary systems containing high-molecular-weight compounds. Figure 4 shows an example of the benzene–polystyrene system. The first evidence in this calculation is that, even if using the group contributions to calculate the pure parameters of a polymer is a strong extrapolation, it seems to work well for all the systems considered; in fact, one binary interaction parameter is enough to obtain an accurate correlation. Moreover, in all cases, the interaction parameter fits well the experimental data at different temperatures. Note that when the same calculations are performed with the pure-polymer parameters derived from the polymer density at a different pressure, as suggested by Song et al. (1994b, 1996), the data fitting in terms of relative pressure deviation is worse than that obtained by using the GC pure-polymer parameter, as reported in Table 4. The reason is because density data do not correctly characterize the EOS energy parameter, which is normally very sensitive to vapor-pressure data.

Note, also, that when GC parameters are used for other systems (Figures 5 and 6), good results are again obtained,

Table 4. Binary-Interaction Parameters vs. Statistical Errors of Six Polymer [1,4-*cis*-polybutadiene, (cPBD); polymethylmethacrylate (PMMA)]-Solvent Systems Obtained from Density Data and GC Estimation

System	Ref.	Polymer MW	T [K]	k_{ij}	AD ($\Delta P/P\%$)	k_{ij}	AD ($\Delta P/P\%$)
				From Density Data		*By Group Contribution*	
PS-benzene	*	63,000	288.15	−0.025	7.28	0.014	3.28
	*	63,000	303.15	−0.025	3.92	0.014	2.53
	*	63,000	318.15	−0.025	4.43	0.014	0.84
	*	63,000	333.15‡‡	−0.025	3.84	0.014	0.62
PS-CH_3Cl	**	1,040	298.15	−0.024	7.67	0.011	6.87
	**	290,000	323.15‡‡	−0.024	1.59	0.011	1.39
PIB-*n*C5	†	1,350	298.15	−0.051	7.53	0.024	2.81
	†	2,700	298.15‡‡	−0.051	7.32	0.024	1.18
PMMA-acetone	††	125,000	323.15‡‡	−0.061	3.59	0.027	2.24
cPBD-CH_3Cl	‡	250,000	333.15‡‡	−0.029	2.81	−0.025	1.09
cPBD-nC_5	‡	250,000	333.15‡‡	−0.055	5.92	0.020	2.92

*Noda et al. (1984).
**Bawn et al. (1956).
†Panayiotou and Vera (1984).
††Tanbonliong and Prausnitz (1997).
‡Gupta and Prausnitz (1995).
‡‡Temperature fitted; all others are predicted.

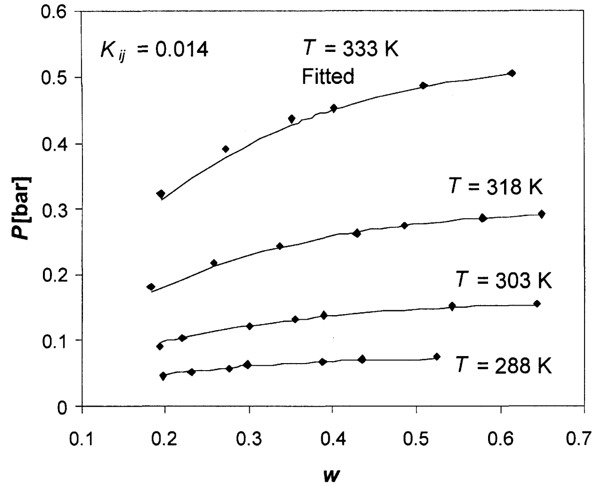


Figure 4. VLE calculation for the binary system benzene-PS.

Data from Noda et al. (1984); w is the weight fraction of benzene.

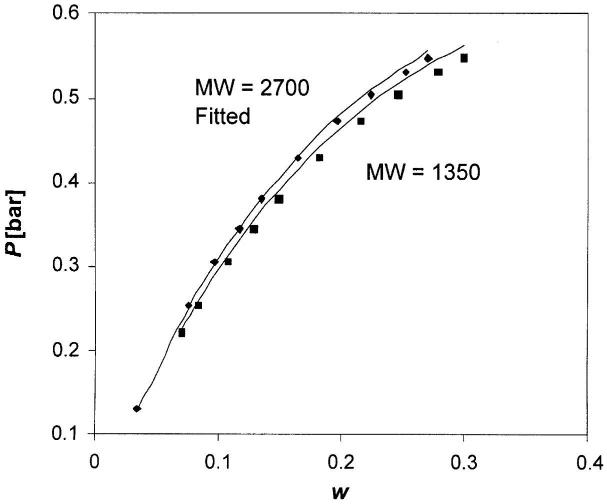


Figure 5. VLE calculation for the binary system pentane-PIB.

Data from Panayotou and Vera (1984); w is the weight fraction of pentane.

and the interaction parameters in all cases have similar and reasonable values. Instead, when pure-polymer parameter values from density data are used, the interaction parameter is larger and its numerical value does not match a regular pattern. Therefore, determination of the pure parameter for a high-molecular-weight substance is crucial, and evidence that the correlation of experimental data by only fitting the binary interaction parameter may not be enough to model these systems.

Table 4 reports the statistical error (absolute deviation) of the correlation of the vapor–liquid equilibria for six different polymer systems obtained with the GC method and with the parameter regressed from density data; in almost all cases there is a consistent reduction of the regression error when GC parameters are used.

Finally, the tables and figures cited show clearly that an accurate prediction is obtained also in the extreme case where the temperature, the molecular weight (and both) are extrapolated (see Figures 4, 5, and 6, respectively).

Figure 7 shows an application of the GC-PHSC to the refrigerant–lubricant oil systems. In the refrigeration systems, a large portion of the problem encountered when the chlorinated working fluid is substituted with hydrofluorocarbons (HFCs) and mixtures of HFCs are related to lubrication problems. From a practical point of view, viscosity and lubricity are very important factors in the performance of the working system, and they depend on the solubility of the working fluid (HFCs) in the compressor oils with different structures. The GC method is applied to calculate the pure parameters for two lubricants: polyolester (POE with a molecular weight of 610) and Pentaerythritol tetra-2-ethylebutanoate (PEB6 with a molecular weight of 528). We note that the EOS parameter characterization could be impossible for lubricant

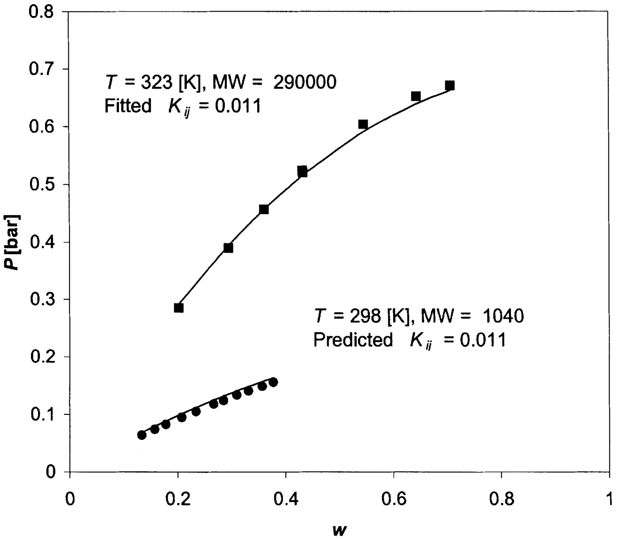


Figure 6. VLE calculation for the binary system chloroform-PS.

PS 1040 MW data from Bawn and Wajid, 1956); PS 290,000 MW data from Panayiotou and Vera (1984); *w* is the weight fraction of chloroform.

oils; the only data available are the molecular structure and the density at room conditions, other properties, such as critical constant, density, and vapor pressure, being unknown.

In Figure 7, the VLE calculations for mixtures containing 1,1,1,2-tetrafluoroethane (HFC134a) and POE or PEB6 over a wide temperature range are obtained using the GC-PHSC EOS with a k_{ij} regressed from the solubility data of HFC134a in PEB6 at 343 K. Figure 7 shows that prediction of the solubility of 1,1,1,2-tetrafluoroethane (HFC134a) at different temperatures and in two lubricant oils that have a similar molecular structure over all range of composition can be achieved with only one temperature-independent binary-interaction parameter.

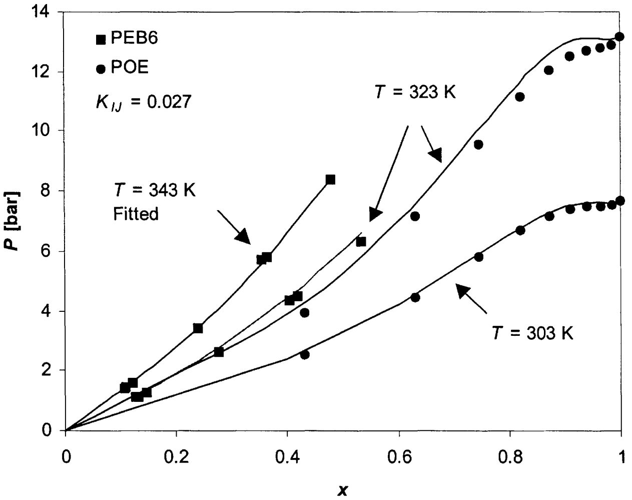


Figure 7. VLE calculation for HFC134a in two lubricant oils at different temperatures.

Squares are experimental data for the system HFC134a-PEB6 (Wahlström and Vamling, 2000), circles are experimental data for the system HFC134a-POE (Takaishi and Oguchi, 1993). Lines are obtained from the GC-PHSC EOS using the K_{ij} fitted to the HFC134a-PEB6 system at 343 K; all other curves are predicted; *x* is the mol fraction of HFC134a.

Liquid–Liquid Equilibria

Once pressure and temperature are specified, the composition of both phases can be determined by solving the equation system that results from the phase-equilibrium criterion. If the configuration of two liquid phases has a lower Gibbs free energy than that of a single-liquid phase, separation will occur. The equilibrium condition is that the chemical potential in the two liquid phases must be equal for all components

$$\Delta \mu_i^a(x_i^a) = \Delta \mu_i^\beta(x_i^\mathrm{B}) \tag{28}$$

where

$$\sum x_i^a = 1 \quad \text{and} \quad \sum x_i^\beta = 1 \tag{29}$$

LLE calculations were performed in two different ways, depending on how big the difference was between the molecular weight of the two components in the system.

In one case, a liquid–liquid isothermal flash calculation program has been implemented following the Michelsen's approach (Michelsen, 1982a,b). In this case, a very good initial estimate of the composition of the two liquid phases for the subsequent flash calculation is provided by the Gibbs tangent-plane stability test (Wasylkiewicz et al., 1996). However, this procedure becomes unreliable for mixtures with large size differences between the solvent and the solute, since the *K*-factors, present in the direct substitution method (Henley and Rosen, 1969, Michelsen, 1982b), are very composition dependent and cause instability in the solution.

A second procedure for the calculation of LLE has been adopted. Thus, good initial estimates of the LLE are generated starting a great distance from the critical point, where convergence is stable and much faster, and then slowly approach the critical zone. The flash calculation has been done by using a decomposition algorithm to simultaneously solve all the flash equations by the Newton–Raphson iterative procedure (Chen et al., 1994).

In order to test the accuracy of the interaction parameters derived from the VLE data, they were used to make a prediction of LLE for some polymer–solvent systems. In this way, results are obtained that are based on the knowledge of the molecular weight, structure, and experimental VLE data of polymer–solvent systems.

We are aware that the simplifying assumptions inherent to the model used, allow only a semiquantitative phenomenological description, and that a more sophisticated theory should be considered to overcome the problems encountered with LLE. In fact, the mean-field approximation model on which the PHSC EOS is based, does not take into account both dilute and concentrate polymer solution regimes. Moreover, the model fails in its description of the equilibrium property, especially near the critical points where the long-range interactions become important. Although results pre-

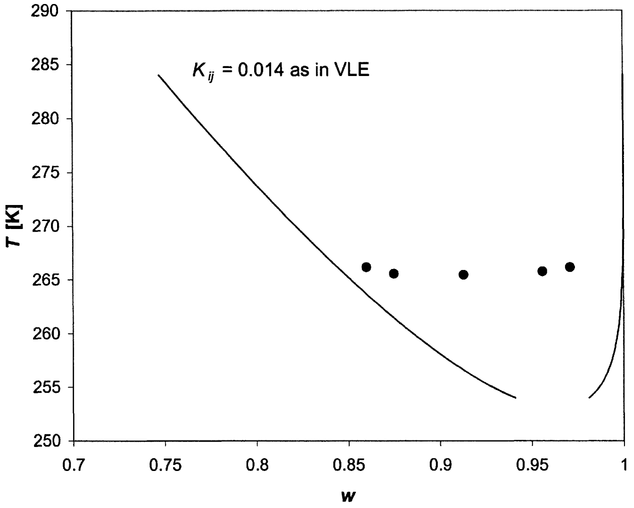


Figure 8. Prediction of LLE calculation for the binary system benzene-PS.

Polymer molecular weight 37,000. Data from Saeki et al. (1974); w is the weight fraction of benzene.

sented in Figures 8 and 9 are not satisfactory, the improvement on the description of these systems when a suitable technique is used to estimate the pure parameter for the high-molecular-weight component is remarkable.

Prediction of LLE was performed for systems exhibiting a lower critical solution temperature (LCST) and an upper critical solution temperature (UCST). In Figure 8, an LCST of the benzene–polystyrene mixture is totally predicted; the LLE is calculated using the interaction parameter regressed from the VLE experimental data. We note that a similar description, by using pure polymer parameters from the density data, is only possible if one adopts k_{ij} values different from the VLE ones plus an additional parameter ν to reduce the number of effective segments in the polymer, as explained by Hino et al. (1996). Otherwise, the phenomenological description of LLE would be completely wrong, and a clessidra diagram would be obtained in spite of two immiscible regions.

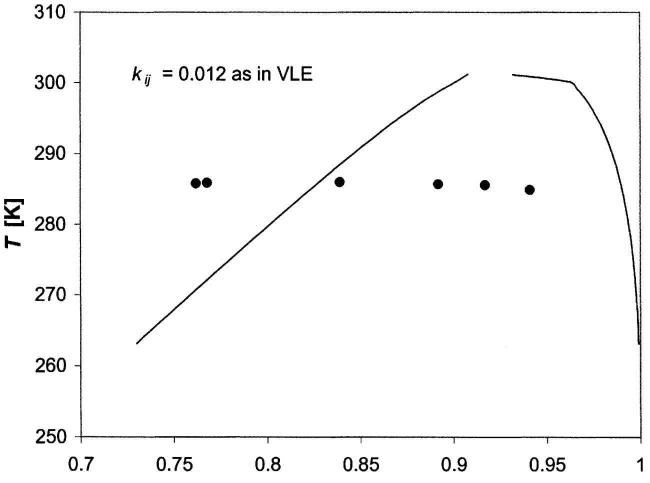


Figure 9. Prediction of LLE calculation for the binary system cycloesane-PS.

Polymer molecular weight is 37,000. Data from Saeki et al. (1973); w is the weight fraction of cycloesane.

In Figure 9 the UCST of the cycloexane–polysterene system is predicted using an interaction parameter $k_{ij} = 0.012$. This value is able to reproduce the VLE experimental data from Schmoll and Jenckel (1956) to within a relative pressure error of 6.7% over the entire composition range and in the 297–313 K temperature range.

It is worthwhile remarking that the perturbation theory upon which the PHSC theory is based, is a mean-field approximation; therefore, the critical regions may not be quantitatively represented by this model. This is especially true for the LLE calculation, where the description of the critical regions is very sensitive to the values of the interaction parameter, k_{ij}. In this case, the LLE predictions using an interaction parameter fitted on VLE experimental data should not be considered to be the general rule. In addition, according to the group contribution idea, neither the different conformational molecular structures of isomers nor the proximity effects of functional groups are taken into account by the GC methods proposed here. However, this work is relevant because it improves the PHSC theory in terms of parameter determination, which allows simulation of the VLE and LLE of mixtures that also contain substances of high molecular weight, for which experimental properties involved in the parameter calculations are often unknown.

Conclusions

A group-contribution method capable of predicting the parameters of the pure compounds of the perturbed hard-sphere-chain equation of state has been developed. Even though this method was devised to solve the problem of determining the molecular parameters for high-molecular-weight compounds in the multicomponent calculation, it also gives satisfactory results for volumetric and pure-component properties. Comparison of the VLE calculations between the method proposed in this work and the traditional parameter-estimation technique proposed by Song et al. (1994b) shows that the new group-contribution method systematically reduces the pressure error in the correlation of the experimental VLE data of the binary systems. The only information required to apply the proposed technique is the structure of the high-molecular-weight compounds in terms of their functional groups. The results reported show that only one interaction parameter, in the case analyzed, is able to correlate VLE data of systems containing a polymer at different temperatures, without any temperature dependence, and throughout the whole composition range. The same interaction parameter also gives a fair phenomenological representation of more thermodynamically complex phenomena, such as LLE.

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