Representation of phase equilibria and densities for complex systems using a van der Waals volume translated equation of state with a UNIFAC mixing rule

Representación del equilibrio de fases y densidades en sistemas complejos, usando la ecuación de estado de Van der Waals, con translación en volumen y regla de mezcla UNIFAC

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ABSTRACT

This work investigated the applicability of the van der Waals cubic equation of state (EoS) with volume translation (vdWt), using the modified Huron-Vidal (MHV2) mixing rule with the UNIFAC (UNIQUAC Functional Activity Coefficients) model for describing phase equilibrium and density data for a series of complex systems over wide ranges of temperature (T) and pressure (P). Some limitations were identified in the prediction of the experimental data collected, e.g., systems with highly associating components, but in general, the EoS vdWt+MHV was able to satisfactorily represent both phase equilibrium and volumetric behavior.

Keywords: Phase equilibrium, equation of state, mixing rule, volume translation, UNIFAC.

RESUMEN

En este trabajo se investigó la aplicabilidad de la ecuación de estado cúbica, de Van der Waals, con translación en volumen (vdWt). Para la regla de mezcla, se aplicó el método de Huron-Vidal modificado (MHV2), con el modelo UNIFAC (UNIQUAC funcional coeficiente de actividad) para describir datos del equilibrio de fases y la densidad para una serie de sistemas complejos; en amplias gamas de temperatura (T) y presión (P). Se encontraron algunas limitaciones en la predicción de los datos experimentales recogidos, por ejemplo, en los sistemas con componentes altamente asociativos, la ecuación vdWt+MHV demostró capacidad para representar de manera satisfactoria, tanto el equilibrio de fases como el comportamiento volumétrico.

Palabras clave: equilibrio de fases, ecuación de estado, regla de mezcla, traslación en volumen y UNIFAC.

Introduction

UNIFAC is a group contribution activity coefficient model whose application as a mixing rule results in a predictive equation of state (EoS) for the desired thermodynamic properties, i.e., density, enthalpy, and phase equilibrium. It is important to note that an EoS may be applied over wide ranges of temperature (T) and pressure (P), which is not possible using activity coefficient models such as UNIFAC because these models are limited by the conditions of the experimental data from which their parameters are estimated, normally low pressures and subcritical components. On the other hand, activity coefficient models are characterized by their capability to describe phase equilibrium data for complex systems due to their mathematical flexibility. Thus, a cubic and simple EoS, combined with the UNIFAC model via the mixing rule, may provide the required tool for predicting thermodynamic properties

valid for various classes of mixtures as well as for wide ranges of T and P. Mixing rules for cubic EoS using group contribution excess free energy models have been studied by various researchers, including Twu et al. (1998), Heidemann (1996), Orbey and Sandler (1996), Novenario et al. (1996), Kalospiros et al. (1995), Kontogeorgis and Folas (2010), Haghtalab and Mahmoodi (2010), Staud and Soares (2012), and Costa et al. (2014). The modified Huron-Vidal mixing rule was introduced by Michelsen (1990), properly matching the excess Gibbs energy calculated by the EoS at zero pressure. This procedure allows for the use of the existing parameters of activity coefficient models that are usually based on experimental data gathered at low pressure.

In this study, the MHV2 mixing rule for the vdW EoS is combined with the UNIFAC model. Several versions of the UNIFAC model

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have been used according to the system studied, i.e., original (Hansen et al., 1991), modified (Larsen et al., 1987) and gas-solvent group (Dahl et al., 1991).

The translation in volume also constitutes an extension of the cubic EoS by an implementation of a volumetric dependency. It is shown in this study that the translated vdW EoS significantly improves the representation of saturated liquid densities. Furthermore, the translation does not affect the phase equilibrium calculation (Péneloux et al., 1982, Meyer, 1987, Tsai and Chen, 1998, Wang and Gmehling, 1999). On the other hand, the calculation of mixture-saturated densities depends on the energy parameter and thereby on the mixing rule adopted, which in this study is the MHV2 mixing rule.

This aim of this work is to systematically evaluate the applicability of the vdWt EoS using the MHV2 mixing rule with UNIFAC for representing phase equilibrium and density data for various complex systems over wide ranges of T and P.

Thermodynamic model

The vdWt EoS is used to represent the desired properties.

$$P = \frac{RT}{(v+t)-b} - \frac{a}{(v+t)^2} = P^{\text{repulsive}} + P^{\text{attractive}} \quad (1)$$

The pure component parameters are calculated from the critical properties according to equation (2).

$$a(T) = a_c \alpha(T_r) = \frac{\Omega_a T_c^2 R^2}{P_c} \alpha(T_r); \ T_r \equiv \frac{T}{T_c}; \ b = \frac{\Omega_b T_c R}{P_c} \quad (2)$$

α is a function of the reduced temperature (T_r). Equation (3) shows the Soave expression applied, where ω is the acentric factor. For subcritical conditions, the Mathias and Copeman (1983) function has been used with coefficients fitted to match the vapor pressure curve; see equation (4) and Table 1.

$$\alpha = \left[1 + C_1\left(1 - \sqrt{T_r}\right)\right]^2; C_1 = 0.486 + 1.624\,\omega - 0.219\,\omega^2; \text{ for } T_r \geq 1 \quad (3)$$

$$\alpha = \left[1 + C_1\left(1 - \sqrt{T_r}\right) + C_2\left(1 - \sqrt{T_r}\right)^2 + C_3\left(1 - \sqrt{T_r}\right)^3\right]^2; \quad T_r < 1 \quad (4)$$

Table 1. Coefficients C_1, C_2 and C_3 from Mathias and Copeman (1983) of pure components for the vdW EoS estimated from the vapor pressure curve[*]

Component	T range (K)	C_1	C_2	C_3	ΔP[†] (%)	ΔP_{max}[‡] (%)
water	300-641	1.1221	-0.7092	0.7179	0.14	0.34
carbon dioxide	216-303	0.8971	-0.5058	1.4440	0.04	0.20
acetic acid	300-580	1.4265	-1.7468	2.1533	0.49	2.08
isobutane	150-400	0.8270	-0.4489	0.9424	0.49	1.13
o-xylene	250-620	1.0571	-0.6362	1.0786	0.35	0.74

[*]100 vapor pressure data points were generated by using the AIChE DIPPR correlation (Daubert and Danner, 1986) over the T range specified.
[†]ΔP: Percent average deviation (100/M Σ|Pexp, i-Pcalc, i|/Pexp, i).
[‡]ΔP_{max}: Percent maximum deviation presented (100 |Pexp, i-Pcalc, i|/Pexp, i).

It is noteworthy that the vdW yields the same degree of vapor pressure correlation as the Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) EoS (Meyer, 1987). This suitable representation of the vdW EoS has also been observed for 438 components (Chiavone-Filho et al., 2001).

The translation function t used herein was developed based on a series of organic and inorganic species of liquid molar volume data and is described as follows (Terron, 2009).

$$t = t_0 + (t_c - t_0)\theta\ ; \quad \theta = 0.7800\,T_r^{9.3931} \quad (5)$$

$$t_0 = 1.0232 + 0.4334 t_c\ ; \ t_c = (3/8 - Z_c)(RT_c/P_c) \quad (6)$$

$$t = t_0 \text{ for } T_r \leq 0.5\ ; \quad t = 0 \text{ for } T_r \geq 1 \quad (7)$$

Table 2 shows the predicted saturated liquid densities for a series of components with four cubic EoS, where the vdWt representation of the experimental points is emphasized.

Table 2. Prediction of saturated liquid densities[*] (ρ) for a series of components using the SRK, PR, vdW and vdWt EoS

Component [T range (K)]	SRK		PR		vdW		vdWt	
	$\Delta\rho$[†] (%)	$\Delta\rho_{max}$[‡] (%)	$\Delta\rho$ (%)	$\Delta\rho_{max}$ (%)	$\Delta\rho$ (%)	$\Delta\rho_{max}$ (%)	$\Delta\rho$ (%)	$\Delta\rho_{max}$ (%)
Water [300-641]	28.3	41.7	19.1	35.6	45.7	49.9	2.1	15.3
Methane [90-185]	4.4	17.1	8.8	12.5	26.8	30.1	1.2	5.5
1,2-Dichloroethane [237-554]	12.4	31.6	2.7	24.0	33.8	41.1	5.7	11.4
Ethanol [230-510]	16.7	32.5	6.0	25.2	37.6	42.4	4.6	7.6
Acetone [190-500]	22.3	33.2	13.4	25.9	42.4	46.3	2.2	6.1
Propane [130-364]	8.3	26.4	5.5	18.4	30.9	36.8	2.7	14.2
Methylcyclohexane [210-570]	10.4	24.0	3.7	16.4	32.5	36.0	0.9	6.8
Ethylbenzene [240-610]	14.1	27.1	3.1	19.3	35.4	39.0	2.0	7.7
n-Decane [260-610]	17.5	31.3	6.9	23.8	38.0	42.0	2.0	7.4
Water [300-641]	28.3	41.7	19.1	35.6	45.7	49.9	2.1	15.3

[*]200 density data points were generated by using the AIChE DIPPR correlation (Daubert and Danner, 1986) over the T range specified.
[†]$\Delta\rho$: Percent average deviation (100/M Σ|ρexp, i-ρcalc, i|/ρexp, i).
[‡]$\Delta\rho_{max}$: Percent maximum deviation presented (100 |ρexp, i-ρcalc, i|/ρexp, i).

The mixing rules define how the EoS parameters are calculated as a function of composition. For the translation (t) and the covolume (b) parameters, the simple linear mixing rule is adequate.

$$b = \sum_i x_i b_i\ ; \quad t = \sum_i x_i t_i \quad (8)$$

For the attractive parameter (a), the conventional quadratic mixing rule presents limitations for systems of species with asymmetry in terms of size, shape and polarity. Michelsen (1990) successfully modified the mixing rule of Huron and Vidal from an infinite-reference pressure to a zero-reference pressure using a function q of the EoS parameters.

$$q\left(\frac{a}{bRT}\right) = \sum_i x_i q\left(\frac{a_i}{b_i RT}\right) + \frac{G^E}{RT} + \sum_i x_i \ln\left(\frac{b}{b_i}\right) \quad (9)$$

This q function provides the adequate matching procedure for the application of the Huron-Vidal mixing rule using activity coefficient models. As explained in the literature (Michelsen, 1990; Dahl and Michelsen, 1990), the function q in its original form presents discontinuities for values of $a/(bRT)$ lower than $3+2\sqrt{2}$. To overcome this limitation, a linear correlation of q was proposed using phase equilibrium data at low pressure in the range of $a_i/(b_i RT)$ values between 7 to 9 for the vdW EoS. More recently, Dahl et al. (1991) applied a quadratic q function, introducing the so-called MHV2 model. In this work, MHV2 is applied for the vdW EoS with the following estimated parameters: q_1=-0.6731 and q_2=-0.0112. Equation (10) describes the MHV2 for the mixture parameter a, which is an implicit expression,

$$q_1\left(\left(a/bRT\right)_{mix} - \sum_i \left(a_i/b_i RT\right)\right) + q_2\left(\left(a/bRT\right)_{mix}^2 - \sum_i \left(a_i/b_i RT\right)^2\right) = \frac{G^E}{RT} + \sum_i x_i \ln\left(b/b_i\right) \quad (10)$$

Methods of calculation

The isofugacity equilibrium criterion is applied via the phi-phi approach, one model for both phases.

$$\hat{f}_i^l = \hat{f}_i^v \Rightarrow \hat{\varphi}_i^l x_i = \hat{\varphi}_i^v y_i \; ; \quad i = 1,2,...N \quad (11)$$

Two types of phase equilibrium calculations were used. The Bubble P calculation is the one in which x_i and T are given and y_i and P are determined. In the *PT*-FLASH mode (Michelsen, 1982; Michelsen and Mollerup, 2007), T, P and z_i (feed concentration) are given to determine x_i and y_i and the concentrations of the two phases. The *PT*-FLASH routine is also applied for liquid-liquid calculation.

The saturated liquid densities are calculated after the determination of the roots of the cubic EoS and are corrected by translation.

$$v_{vdWt} = v_{vdW} + t \Rightarrow \quad \rho = \frac{1}{v_{vdWt}} \quad (12)$$

Results and final remarks

A representative series of experimental data for vapor-liquid equilibrium (VLE) and saturated liquid density (ρ) were selected for various systems and conditions to evaluate the prediction ability of the present vdWt+MHV2 EOS; see Table 3.

Table 3. vdWt + MHV2 predictions of VLE and saturated liquid densities

System	T (K)	P (bar)	dtpts*	dev†(%)	Reference
carbon dioxide + isopentane‡	278	0.4-39	10/VLE 10/ρ	ΔP=5.4 Δρ=0.4	Besserer and Robinson (1975)
n-hexane + 1-propanol#	308-318	0.1-1	5/VLE 10/ρ	ΔP=1.2 Δρ=1.4	Brow et al. (1969) Ormanoudis et al. (1991)
n-butane + 1,1,2-trichloro-1,2,2-trifluoretane#	363-423	3.4-36	12/VLE 12/ρ	ΔP=0.8 Δρ=1.0	Laugier et al. (1994)
1,1,2-trichloro-1,2,2-trifluorethane + heptane#	363-408	0.7-9.8	16/VLE 16/ρ	ΔP=1.1 Δρ=1.1	Laugier et al. (1994)
hydrogen sulfide + hexane‡	323-423	0.5-85	24/VLE	ΔP=3.7	Laugier and Richon (1995)
acetone + methanol + water#	373	1.2-4	51/VLE	ΔP=7.0	Griswold and Wong (1952)
water + isobutane + 2-propanol#	319-364	6-17.1	9/VLE	ΔP=1.9	Zabaloy et al. (1993)
System	T (K)	P (bar)	dtpts*	dev†(%)	Reference

*Number and type of data points.
†Percent average deviation (100/M Σ|expi-calci|/expi).
‡Modified (Larsen et al., 1987) and gas-solvent group (Dahl et al., 1991) UNIFAC tables have been used.
#Original UNIFAC tables have been used (Hansen et al., 1991).

Liquid-liquid equilibrium (LLE) data representation for some ternary systems, such as water + acetic acid + isoamyl alcohol, was also studied. Figure 1 demonstrates the LLE behavior predicted by the vdWt+MHV2 for the mixture water + ethanol + toluene, which is as good as the UNIFAC (Peschke and Sandler, 1995).

Figures 2 and 3 present the good phase equilibrium and density data predictions yielded by the vdWt+MHV2 EoS for the butane + 1,1,2-trichloro-1,2,2-trifluorethane system. The H2S + hexane system was also studied under supercritical conditions, and the

vdWt+MHV2 EoS was determined to provide satisfactory representation; see Figure 4.
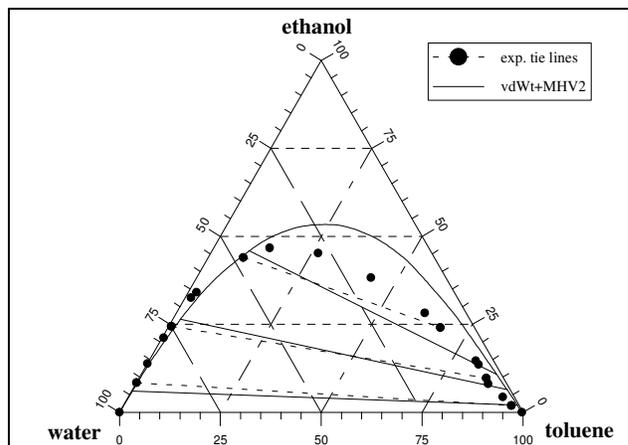
Figure 1. vdWt+MHV2 prediction of the LLE data for the water + ethanol + toluene system at 298 K and 1.013 bar. Axes are in mole percent. Experimental data presented by Peschke and Sandler (1995).
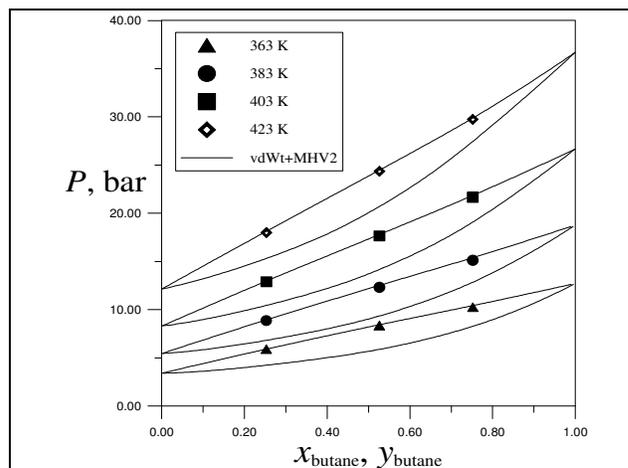
Figure 2. Diagram of pressure versus composition for *n*-butane + 1,1,2-trichloro-1,2,2-trifluorethane. Experimental data obtained by Laugier et al. (1994).
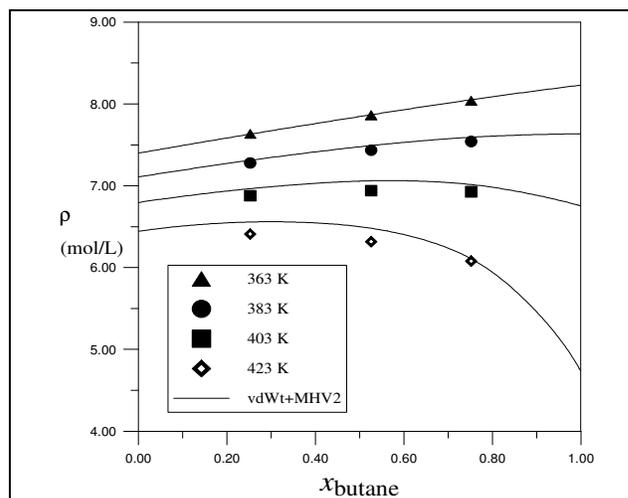
Figure 3. Saturated liquid density versus composition for *n*-butane + 1,1,2-trichloro-1,2,2-trifluorethane. Experimental data obtained by Laugier et al. (1994).
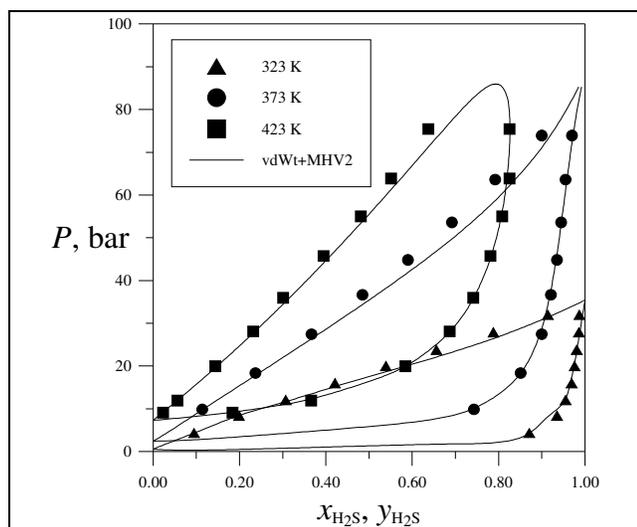
Figure 4. Representation of the VLE data for the H₂S + *n*-hexane system (Laugier and Richon, 1995).

Some limitations in the prediction of the experimental data collected were identified, e.g., systems with highly associative components and with significant asymmetry. In particular, the systems carbon dioxide + isopentane and acetone + methanol + water presented higher deviations for the vdWt+MHV2 VLE data description. For the liquid density representation, polar species such as 1,2-dichloroethane and ethanol showed more pronounced deviations from the vdWt EoS. To overcome these limitations, association and more rigorous repulsive terms should be considered in the thermodynamic model (Kalospiros et al., 1995; Kontogeorgis and Folas, 2010). However, in general, the EoS vdWt+MHV2 was able to satisfactorily represent both phase equilibrium and volumetric behavior. The translation in volume expression proposed in this work can be extended to a more comprehensive series of pure substances using available data. In addition, it would be advantageous to have a continuous translation function, valid for wide ranges of T and P. The mixing rule is limited to the UNIFAC parameters; however, as shown by Dahl et al. (1991) and more recently by Haghtalab and Mahmoodi (2010), interaction parameters for supercritical components can be estimated by correlating gas solubility data, thereby extending the application of the EoS. The flexibility and predictive character of the vdWt+MHV2 is found to be a simple but powerful simple tool for calculating thermodynamic properties. Furthermore, the vdWt+MHV2 may be applied in a process simulator.

Acknowledgment

Nomenclature

AIChE	American Institute of Chemical Engineers
a	Attractive parameter
b	Covolume parameter
a/(*bRT*)	Dimensionless parameter; argument of the q function in equation (9)
C_i	Mathias and Copeman (1983) coefficients to express α as a function of the reduced temperature, see equation (4)
Dev	Deviation

DIPPR	Design Institute for Physical Properties
dtpts	Number and type of data points, see Table 3
EoS	Equation(s) of State
G	Gibbs free energy
LLE	Liquid-liquid equilibrium
MHV2	Modified Huron-Vidal mixing rule with quadratic approximation for the q function
M	Total number of data points
N	Total number of components
P	Pressure
PR	Peng-Robinson
q	Function of $a_i/(b_iRT)$ in the MHV mixing rule
q_i	Coefficients of the q function in the MHV mixing rule
R	Universal gas constant
SRK	Soave-Redlich-Kwong
T	Absolute temperature
t	Translation parameter or function
t_i	Translation coefficients, see equations (5) and (6)
v	Molar volume
vdW	van der Waals
vdWt	van der Waals translated or with volume translation
VLE	Vapor-liquid equilibrium
x	Mole fraction of the liquid phase
y	Mole fraction of the vapor phase
Z	Compressibility factor
z	Mole fraction of the feed in the Flash calculation

Greek Letters

α	Alpha function expressing the dependence of the attractive parameter on the reduced temperature; see equation (4)
ρ	Liquid molar density
φ	Fugacity coefficient
θ	Theta function expressing the dependence of the translation parameter on the reduced temperature; see equation (5)
ω	Acentric factor

Superscripts and Subscripts

c	Critical property
calc	Calculated value
E	Excess property
exp	Experimental value
L	Liquid phase
max	Maximum
r	Reduced property
V	Vapor phase
^	Property of component *i* in the mixture

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