ELSEVIER

Chemical Engineering Journal 79 (2000) 87–101

Chemical Engineering Journal

www.elsevier.com/locate/cej

Equation of state associated with activity coefficient models to predict low and high pressure vapor–liquid equilibria

Otilio Hernández-Garduza[a,*], Fernando García-Sánchez[a], Evelyne Neau[b], Marek Rogalski[c]

[a] *Grupo de Simulación Molecular, Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, 07730 México D.F., Mexico*
[b] *Laboratoire de Chimie Physique, Faculté des Sciences de Luminy, 13288 Marseille Cedex 9, France*
[c] *Laboratoire de Thermodynamique Chimique et Appliquée, INPL−ENSIC, B.P. 451, 54001 Nancy, France*

Received 9 November 1998; received in revised form 14 January 2000; accepted 21 January 2000

Abstract

A simple and thermodynamically consistent method is presented to establish an equation of state for mixtures by using activity coefficient model parameters. All current solution models such as NRTL, van Laar, UNIFAC, or any other thermodynamic model can be used. The main feature of the method presented is that only a single scaling factor value determined at a given reference temperature is required to predict the vapor–liquid equilibria in a wide range of temperature and pressure. The performance of the method is tested on the prediction of the vapor–liquid equilibria at low, moderate, and high pressures for six binary systems (methanol−benzene, acetone−water, methanol−acetone, methanol−water, ethanol−water, and 2-propanol−water) and a ternary system (acetone−water−methanol). For comparison, vapor–liquid equilibrium calculations were carried out with the Wong and Sandler method by using the PRSV equation of state associated with the van Laar and scaling factors. On the whole, it is found that at high pressures both methods give similar predictions but at low pressures the proposed method gives sometimes better results than that of Wong and Sandler method. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Equation of state; Activity coefficient model; Vapor–liquid equilibria; Scaling factor

1. Introduction

Using equations of state associated with excess function models usually perform the representation of thermodynamic properties of mixtures at high temperatures and pressures (see [1–23]). Huron and Vidal [1], who pointed out the relation existing between equation of state mixing rules and the excess free energy models, initiated this development. In particular, these authors derived their equations for the dense fluid (infinite pressure reference) of the equation of state. Therefore, equations of state derived from this formalism make possible to correlate phase equilibria at high temperatures; however, a drawback of this procedure is that the parameters of the excess Gibbs free models must be fitted to experimental data at high temperatures. That is, it is impossible to simply insert excess free models regressed from low-pressure data into equation of state mixing rules without refitting the model parameters.

Later, Mollerup [2] suggested a method of associating an equation of state to excess functions with reference to the zero pressure. With this formalism, it was possible to directly use the parameters of the excess Gibbs model determined at low pressures but the extension of these models to high pressures was no longer satisfactory. Since then, many efforts have been devoted to the development of methods allowing the extrapolation toward high pressures of models depending on parameters determined at low-pressure ranges. In other words, it is necessary to determine a ‘scaling factor’ between the excess function model and the equation of state considered.

Thus, Gupte and Daubert [3] and Gani et al. [4] considered the van der Waals equation of state associated with the UNIFAC model (cf. [24]) and a volume-dependent scaling factor. Michelsen [6,7] applied the Soave–Redlich–Kwong [25] equation of state together with the Wilson model having a temperature-dependent scaling factor. Similarly, Heidemann and Kokal [8] proposed to associate cubic equations of state with the NRTL model [26] and a scaling factor determined at low pressure. More recently, Wong and Sandler [13] used the Peng–Robinson [27] equation of state, as applied by Stryjek and Vera [28], in conjunction with the NRTL model and a scaling factor introduced in the second virial coefficient expression. Nevertheless, it should be mentioned that any combination of excess Gibbs free energy functions with equations of state using Vidal based mixing rules, does not reproduce the ideal solution. Therefore, as shown by

---

[*] Corresponding author. Fax: +52-5-368-9203.

PII: S1385-8947(00)00138-8

Wilczek-Vera and Vera [29], to obtain ideal behavior, excess Gibbs free functions different from zero are required.

In this work, we have considered the formalism of equations of state associated with excess function models with reference to the constant packing fraction as defined by Péneloux et al. [30]. This formalism, based on the lattice model in the zeroth approximation, is considered to be more general since it can be applied either to cubic or non-cubic equations of state and stands between the limits of zero and infinite pressure. Consequently, we propose a simple method for utilization of activity coefficient models in which the parameters are estimated at low pressure and at a single temperature. The scaling factor considered here takes into account the limit of the excess Gibbs model at infinite pressure.

In order to test the proposed method, it was applied to the prediction of vapor–liquid equilibria of binary and ternary systems at low and high pressures by using the van Laar, NRTL, and the modified UNIFAC [31] activity coefficient models. The results obtained on binary mixtures were compared to those obtained by using the method of Wong et al. [13].

2. Formulation of the problem and approach proposed

In the formalism of equations of state associated to an excess function model with reference to the constant packing fraction, $\eta = b/v$, the compressibility factor, z, of a mixture containing p compounds is written as

$$z(T,\eta,\boldsymbol{x}) = \sum_{i=1}^{p} x_i z_i(T,\eta) + z^{\mathrm{E}}(T,\eta,\boldsymbol{x}) \tag{1}$$

where z_i is the compressibility factor of pure component i, calculated for the mixture packing fraction, $\eta = b/v$, and z^{E} is the excess compressibility factor estimated from the excess Helmholtz free energy, A^{E}, which can be written as

$$z^{\mathrm{E}}(T,\eta,\boldsymbol{x}) = \eta \left[\frac{\partial A^{\mathrm{E}}(T,\eta,\boldsymbol{x})/RT}{\partial \eta}\right]_{T,\boldsymbol{x}} \tag{2}$$

with

$$A^{\mathrm{E}}(T,\eta,\boldsymbol{x}) = \left[A(T,\eta,\boldsymbol{x}) - A^{*}(T,\eta,\boldsymbol{x})\right] - \sum_{i=1}^{p} x_i \left[A_i(T,\eta) - A_i^{*}(T,\eta)\right] \tag{3}$$

where A and A^{*} are the Helmholtz free energy of the mixture and that corresponding to the ideal gas state, respectively, while A_i and A_i^{*} are the Helmholtz free energy of pure component i and that corresponding to the ideal gas state.

The expression of the compressibility factor given by Eq. (1) is a general one, since any type of equation of state can be used for each pure component. For instance, in mixtures of carbon dioxide with n-alkanes, Rauzy and Péneloux [32] used the IUPAC [33] equation for carbon dioxide and the Peng–Robinson [27] equation of state for n-alkanes. Besides, Solimando et al. [34], in a comparative study of several equations of state derived from the van der Waals theory, selected models able to represent PVT properties of hydrocarbons of various sizes and structures in large pressure and temperature ranges. Experimental data of vapor–liquid equilibria (vapor pressures and liquid volumes) and PVT properties of compressed fluids were systematically compared with results obtained using selected equations of state. These authors showed that only the complex equations of state (especially the Chain of Rotators [35] equation) are able to represent volumetric properties in wide temperature and pressure ranges, including the critical region.

It is worth noting that the constant packing fraction reference does not lead to zero mixing volumes since the compressibility factors of pure compounds, z_i, are estimated for the packing fraction of the mixture at the given temperature and pressure and not for the pure-component packing fraction, η_i, at the same temperature. Thus, in the formalism of equations of state associated with excess functions using the reference packing fraction, the compressibility factor of a mixture at p components is written as

$$z = \frac{1}{1-\eta} - \sum_{i=1}^{p} x_i \frac{a_i}{b_i RT} Q'(\eta) + z^{\mathrm{E}} \tag{4}$$

where $Q'(\eta)$ is the packing fraction function depending on the equation of state considered. Since the excess compressibility factor, z^{E}, depends on both the composition and the packing fraction, then we can express z^{E} as follows:

$$z^{\mathrm{E}} = \frac{E(T,\boldsymbol{x})}{RT} F(\eta) \tag{5}$$

where $E(T,\boldsymbol{x})$ is the excess free energy which can be expressed with any of the classical forms of the excess functions (e.g. van Laar, NRTL, UNIQUAC, UNIFAC) or derived from a given mixing rule. Of course, it is important to mention that several expressions for the packing fraction function $F(\eta)$ can be chosen under the condition that its extrapolation toward the zero value of the packing fraction must satisfy the virial development. This procedure was also used by Lermite and Vidal [36] with the Simonet–Behar–Rauzy [37] equation of state and by Solimando et al. [38] with an augmented version of the Peng–Robinson equation of state.

In this work, the one-fluid model is considered in the formulation of the method in such a way that the function $F(\eta)$ is equal to $Q'(\eta)$. On this basis, the compressibility factor can be written as

$$z = \frac{1}{1-\eta} - \frac{a}{bRT} Q'(\eta) \tag{6}$$

where

$$\frac{a}{b} = \sum_{i=1}^{p} x_i \frac{a_i}{b_i} - E(T,\boldsymbol{x}) \tag{7}$$

and

$$b=\sum_{i=1}^{p}x_i b_i \tag{8}$$

A detailed description of the compatibility between the reference state at constant packing fraction and its limit to high pressure and temperature, and that at infinite pressure [1], is given in Appendix A.

By introducing the following function into Eq. (6)

$$Q'(\eta)=\frac{\eta}{(1+c_1\eta)\,(1+c_2\eta)} \tag{9}$$

we can get different cubic equations of state depending on the values of the constants c_1 and c_2. Thus, for example, with c_1=0 and c_2=1, the Redlich–Kwong [39] equation of state is obtained.

In this work, the Peng–Robinson equation of state expressed in terms of a translated volume with c_1=0 and $c_2=2+2\sqrt{2}$, as suggested by Rauzy [40], was used along the equilibrium calculations. However, it is well known that an excellent correlation of the pure-component vapor pressures is a requirement for accurate prediction of the vapor–liquid equilibria of mixtures. Hence, the temperature-dependent function of equation of state energy parameter a must be carefully chosen to reproduce pure-component vapor pressures. Consequently, we have chosen the Carrier–Rogalski–Péneloux [41] correlation for function $a(T)$ in our calculations. We refer to this as the translated PRCRP equation of state, and it is given in Appendix B.

It is worthwhile pointing out that the choice of the van Laar model for the excess function $E(T,\boldsymbol{x})$, given in Eq. (7), is equivalent to the use of the classical quadratic mixing rules with a single binary interaction parameter. Indeed, there is equivalence in using the expression

$$E(T,\boldsymbol{x})=\frac{1}{2}\sum_{i=1}^{p}\sum_{j=1}^{p}x_i x_j\frac{b_i b_j}{b}E_{ij},\qquad E_{ji}=E_{ij},\quad E_{ii}=0 \tag{10}$$

or the quadratic mixing rule,

$$a=\sum_{i=1}^{p}\sum_{j=1}^{p}x_i x_j\sqrt{a_i a_j}(1-k_{ij}),\quad k_{ji}=k_{ij},\quad k_{ii}=0 \tag{11}$$

with the following correlation between parameters:

$$E_{ij}=(\delta_i-\delta_j)^2+2\delta_i\delta_j k_{ij},\qquad \delta_i=\frac{\sqrt{a_i}}{b_i} \tag{12}$$

We can also note that the van Laar model, Eq. (10), is a unique model that allows obtention of the correct quadratic form for the second virial coefficient:

$$B(T)=b-\frac{a}{RT} \tag{13}$$

2.1. Proposed expression for the excess free energy *E(T,* $\boldsymbol{x}$*)*

The expression for the excess Gibbs free energy we propose in this work is based on the model of Péneloux et al. [30] at constant packing fraction and on the compatibility with the Huron and Vidal's based mixing rules [1] at very high temperatures and pressures.

For a binary mixture, Eq. (7) can be applied by using the following relation for the excess free energy:

$$\frac{E(T,x_1,x_2)}{RT}=x_1\frac{\ln\gamma_1(T_{12}^0,x_1,x_2)}{\lambda_{12}(T)}+x_2\frac{\ln\gamma_2(T_{12}^0,x_1,x_2)}{\lambda_{21}(T)},\qquad \lambda_{21}=\lambda_{12} \tag{14}$$

where $\gamma_1(T_{12}^0,\boldsymbol{x})$ and $\gamma_2(T_{12}^0,\boldsymbol{x})$ are the activity coefficients of components 1 and 2, respectively, evaluated at the reference temperature T_{12}^0, and $\lambda_{12}(T)$ is the binary temperature-dependent scaling factor which is given by

$$\frac{1}{\lambda_{12}(T)}=\frac{1+\beta_{12}/T}{\lambda_\infty} \tag{15}$$

with

$$\beta_{12}=\frac{(\lambda_\infty-\lambda_{12}^0)T_{12}^0}{\lambda_{12}^0} \tag{16}$$

where λ_{12}^0 is the scaling factor which, using an equation of state, allows a satisfactory representation of vapor–liquid or liquid–liquid phase equilibrium data at the reference temperature T_{12}^0, and λ_∞ is the limit value of λ_{12} at infinite temperature.

It is important to notice that to find the Huron–Vidal formalism at high temperature and pressure, the scaling factor λ_∞ is equal to the function $Q(\eta=1)$, (see Eq. (A.2)). According to Eq. (14), it can be seen that the activity coefficients, γ_i, used for the calculation of the excess function $E(T,\boldsymbol{x})$, are independent of the temperature other than T_{12}^0.

In the case of mixtures with p components, Eq. (14) cannot be directly extrapolated since the activity coefficient of component i takes into account the interactions between component i with all other components $j,k,\ldots$, so that the corresponding scaling factors $\lambda_{ij},\lambda_{ik},\ldots$ are usually different, even at the same reference temperature T^0. In order to overcome this problem, the following two procedures were considered:

For models such as the van Laar or the NRTL equation, in which the activity coefficient of component i, $\ln\gamma_i$, is expressed by a sum extended over all the binary interactions parameters, the excess free energy can be written as:

2.1.1. van Laar model

$$\frac{E(T,\boldsymbol{x})}{RT}=\frac{1}{2}\sum_{i=1}^{p}x_i\frac{\sum_{j=1}^{p}x_j(A_{ji}^0/\lambda_{ji})}{\sum_{k=1}^{p}x_k C_{ki}^0} \tag{17}$$

and

$$\frac{\ln\gamma_i}{\lambda(T)}=\frac{1}{2}\frac{\sum_{j=1}^{p}x_j(A_{ji}^0/\lambda_{ji})}{\sum_{k=1}^{p}x_kC_{ki}^0}+\frac{1}{2}\sum_{j=1}^{p}\frac{x_j}{\sum_{k=1}^{p}x_kC_{kj}^0}\times\left[\frac{A_{ij}^0}{\lambda_{ij}}-C_{ij}^0\frac{\sum_{m=1}^{p}x_m(A_{mj}^0/\lambda_{mj})}{\sum_{k=1}^{p}x_kC_{kj}^0}\right]\tag{18}$$

with

$$C_{ij}^0=\frac{A_{ij}^0}{A_{ji}^0},\qquad C_{ii}^0=C_{jj}^0=1,\qquad A_{ii}^0=A_{jj}^0=0,$$
$$\lambda_{ji}=\lambda_{ij}=\lambda_{ij}(T)\tag{19}$$

where A_{ij}^0 and A_{ji}^0 are the van Laar binary parameters at the corresponding temperatures T_{ij}^0.

2.1.2. NRTL model

$$\frac{E(T,\boldsymbol{x})}{RT}=\sum_{i=1}^{p}x_i\frac{\sum_{j=1}^{p}x_jG_{ji}^0(\tau_{ji}^0/\lambda_{ji})}{\sum_{k=1}^{p}x_kG_{ki}^0}\tag{20}$$

and

$$\frac{\ln\gamma_i}{\lambda(T)}=\frac{\sum_{j=1}^{p}x_jG_{ji}^0(\tau_{ji}^0/\lambda_{ji})}{\sum_{k=1}^{p}x_kG_{ki}^0}+\sum_{j=1}^{p}\frac{x_jG_{ii}^0}{\sum_{k=1}^{p}x_kG_{kj}^0}\times\left[\frac{\tau_{ij}^0}{\lambda_{ij}}-\frac{\sum_{m=1}^{p}x_mG_{mj}^0(\tau_{mj}^0/\lambda_{mj})}{\sum_{k=1}^{p}x_kG_{kj}^0}\right]\tag{21}$$

with

$$G_{ij}^0=\exp(-\alpha_{ij}^0\tau_{ij}^0),\qquad \tau_{ij}^0=\frac{(g_{ij}^0-g_{jj}^0)}{RT_{ij}^0},$$
$$\tau_{ji}^0=\frac{(g_{ji}^0-g_{ii}^0)}{RT_{ij}^0},\qquad \lambda_{ji}=\lambda_{ij}=\lambda_{ij}(T),\qquad \alpha_{ji}^0=\alpha_{ij}^0,$$
$$G_{ii}^0=G_{jj}^0=1,\qquad \tau_{ii}^0=\tau_{jj}^0=0\tag{22}$$

where $(g_{ij}^0-g_{jj}^0)$, $(g_{ji}^0-g_{ii}^0)$, and α_{ij}^0 are the NRTL binary parameters at the reference temperature T_{ij}^0.

For other models, such as the UNIFAC equation, in which each term of the activity coefficient, $\ln\gamma_i$, is divided by the mean value $\bar{\lambda}_i$ of all the binary scaling factors λ_{ij} involved in the mixture, the excess free energy can be expressed as:

2.1.3. UNIFAC model

$$\frac{E(T,\boldsymbol{x})}{RT}=\sum_{i=1}^{p}x_i\frac{\ln\gamma_i(T^0,\boldsymbol{x})}{\bar{\lambda}_i(T)}\tag{23}$$

where

$$\ln\gamma_i(T^0,\boldsymbol{x})=\ln\gamma_i^{\rm C}(\boldsymbol{x})+\ln\gamma_i^{\rm R}(T^0,\boldsymbol{x})\tag{24}$$

$\gamma_i^{\rm C}$ and $\gamma_i^{\rm R}$ being defined by the UNIFAC model [31].

3. Application of the approach

The method proposed in this work was applied to the representation of vapor–liquid equilibria using the translated PRCRP equation of state associated with the van Laar, NRTL and modified UNIFAC activity coefficient models. Calculations were performed using the interaction parameters taken from the DECHEMA Chemistry Data Series (see [42–44]) for the van Laar and NRTL models and from Gmehling et al. [31] for the modified UNIFAC model. Relevant pure-component properties used in this study are given in Table 1.

The binary mixtures studied to test our approach were the methanol–benzene, acetone–water, acetone–methanol, water–methanol, water–ethanol, and water–2-propanol systems. The interest of these systems, frequently studied by other investigators, is due to the fact that there are many

Table 1
Pure-component properties and parameters m_0, m_1 and m_2 used in the translated PRCRP equation of state

Component	T_c (K)	P_c (bar)	T_b (K)	m_0	m_1	m_2	$T_{\min}-T_{\max}$ (K)	dP/p (%)	N_b	Reference
Benzene	562.15	48.970	353.24	0.68993	2.25148	0.62126	287.70–354.07	0.04	19	[45]
							294.16–378.15	0.05	19	[46]
Acetone	508.15	47.015	329.20	0.81844	1.68549	0.27537	310.83–329.17	0.02	8	[47]
							273.05–328.43	0.05	13	[48]
Methanol	512.65	80.959	337.70	1.15812	1.15727	−0.13199	288.05–356.83	0.05	20	[49]
							274.87–336.53	0.15	15	[50]
							288.15–337.65	0.07	18	[51]
							262.59–356.03	0.04	25	[52]
Ethanol	513.92	61.370	351.44	1.27246	1.63796	−0.05154	273.15–351.70	0.14	8	[53]
							293.15–323.15	0.06	6	[54]
							292.77–366.63	0.04	25	[49]
							276.50–370.50	0.15	27	[52]
2-Propanol	508.40	47.642	355.76	1.30622	2.84267	0.43359	354.76–420.78	1.62	17	[55]
							275.64–373.45	0.87	27	[52]
							325.47–362.41	1.05	17	[49]
Water	647.37	221.200	373.15	0.85710	1.35795	0.16530	273.15–373.15	0.01	52	[56]

Table 2
Vapor–liquid equilibrium deviations on pressure, $\delta P/P$, and on vapor mole fractions, δy, using the translated PRCRP equation of state associated with activity coefficient models[a]

System	van Laar			NRTL			UNIFAC			T_{12}^0 (K)
	$\delta P/P^b$ (%)	δy^c	λ_{12}^0	$\delta P/P^b$ (%)	δy^c	λ_{12}^0	$\delta P/P^b$ (%)	δy^c	λ_{12}^0	
Methanol−benzene	2.04	0.012	0.25	2.19	0.012	0.25	0.70	0.007	0.28	373.15
Acetone−water	3.27	0.014	0.22	3.37	0.014	0.22	4.22	0.018	0.22	373.15
Methanol−acetone	1.60	0.022	0.31	1.60	0.022	0.31	1.20	0.012	0.28	373.15
Methanol−water	1.40	0.010	0.23	1.42	0.010	0.23	2.54	0.009	0.27	373.15
Ethanol−water	1.16	0.005	0.23	1.15	0.005	0.23	1.61	0.008	0.23	343.15
2-Propanol−water	2.52	0.028	0.22	1.83	0.024	0.22	2.05	0.035	0.22	333.15

[a] Scaling factors λ_{12}^0 determined at the reference temperature T_{12}^0; data taken from DECHEMA Data Series [42–44].

[b] $\delta P/P=(100/N_\mathrm{p})\sum_{i=1}^{N_\mathrm{p}}\left|(P_i^{\mathrm{exp}}-P_i^{\mathrm{calc}})/P_i^{\mathrm{exp}}\right|$.

[c] $\delta y=1/N_\mathrm{p}\sum_{i=1}^{N_\mathrm{p}}\left|y_i^{\mathrm{exp}}-y_i^{\mathrm{calc}}\right|$.

Table 3
High-pressure vapor–liquid equilibrium deviations on pressure, $\delta P/P$, and on vapor mole fractions, δy, for binary mixtures using the Wong–Sandler and the proposed methods

System	T (K)	N_p	Wong–Sandler		This work					
			van Laar		van Laar		NRTL		UNIFAC	
			$\delta P/P$	δy	$\delta P/P$	δy	$\delta P/P$	δy	$\delta P/P$	δy
Methanol−benzene	373.15	12	4.47	0.022	2.04	0.012	2.19	0.012	0.70	0.007
	413.15	12	1.76	0.010	4.53	0.022	4.56	0.023	5.36	0.014
	453.15	12	0.98	0.015	7.38	0.031	7.41	0.032	8.36	0.029
	493.15	12	2.60	0.033	5.38	0.058	5.42	0.058	5.30	0.059
	Total	48	2.45	0.020	4.83	0.031	4.89	0.031	4.93	0.027
Acetone−water	373.15	22	2.80	0.007	3.27	0.014	3.37	0.014	4.22	0.019
	423.15	17	2.25	0.009	2.84	0.016	2.88	0.016	3.02	0.022
	473.15	25	1.03	0.007	1.70	0.015	1.78	0.015	2.98	0.020
	523.15	17	1.38	0.012	1.37	0.012	1.49	0.012	1.26	0.014
	Total	81	1.84	0.008	2.30	0.014	2.38	0.014	2.96	0.019
Methanol−acetone	373.15	14	1.91	0.015	1.60	0.022	1.60	0.022	1.20	0.012
	423.15	15	0.80	0.019	0.72	0.021	0.76	0.021	1.40	0.016
	473.15	10	2.52	0.033	2.79	0.033	2.89	0.033	3.59	0.031
	Total	39	1.64	0.021	1.57	0.024	1.61	0.024	1.89	0.018
Methanol−water	373.15	16	1.36	0.009	1.40	0.010	1.42	0.010	2.54	0.009
	423.15	14	2.08	0.013	1.72	0.014	1.59	0.014	1.96	0.017
	473.15	15	1.17	0.010	1.42	0.009	1.30	0.008	1.44	0.009
	523.15	12	1.48	0.019	2.08	0.013	1.85	0.012	1.26	0.010
	Total	57	1.51	0.012	1.63	0.011	1.52	0.011	1.84	0.011
Ethanol−water	423.15	17	3.86	0.017	1.78	0.011	1.82	0.010	2.29	0.014
	473.15	17	2.25	0.007	1.39	0.010	1.47	0.011	1.92	0.013
	523.15	16	1.13	0.008	0.95	0.009	0.99	0.008	1.02	0.009
	548.15	11	2.01	0.017	1.33	0.009	1.39	0.009	1.09	0.010
	573.15	7	1.73	0.015	0.57	0.010	0.50	0.010	0.68	0.012
	598.15	7	2.12	0.017	0.95	0.003	0.87	0.003	0.47	0.003
	623.15	4	0.36	0.003	0.23	0.002	0.30	0.002	0.48	0.003
	Total	79	2.18	0.012	1.21	0.009	1.24	0.09	1.39	0.011
2-Propanol−water	423.15	19	1.81	0.016	2.53	0.024	2.81	0.028	4.84	0.030
	473.15	18	1.40	0.016	1.90	0.017	2.54	0.021	4.33	0.023
	523.15	13	4.94	0.025	1.35	0.016	1.27	0.019	1.52	0.022
	548.15	18	6.98	0.035	1.91	0.019	1.11	0.023	1.22	0.022
	573.15	6	4.68	0.042	1.33	0.043	0.93	0.045	1.19	0.045
	Total	74	3.75	0.024	1.93	0.021	1.91	0.025	2.96	0.026

phase equilibrium data reported at low and high pressures, which allows accuracy of the predictive methods to be tested. In addition, the prediction of the vapor–liquid equilibria for the ternary mixture acetone–methanol–water is also considered.

3.1. Vapor–liquid equilibria at the reference temperature

The reference temperature, T_{12}^0, used for each binary system studied is given in Table 2 together with the values of the scaling factor λ_{12}^0, which were determined from vapor–liquid equilibrium data at this temperature. The deviations obtained between experimental and calculated vapor pressures and mole fractions are also reported in the same table.

Through an examination of the results, the following observations are made. Firstly, for the three models considered, the deviations on pressures and mole fractions from experimental data are quite small in such a way that it is possible to obtain a satisfactory representation of the vapor–liquid equilibria using the proposed method with reported activity coefficient parameters. Secondly, it can be seen that in all the cases, the value of λ_{12}^0 was lower than the scaling factor λ_∞ estimated at infinite pressure reference (i.e. $\lambda_\infty \approx 0.365$). Comparable values of λ_{12}^0, except for the system methanol–acetone ($\lambda_{12}^0 = 0.31$), were obtained with the van Laar and NRTL models. That is, the scaling factors were approximately of the same order of magnitude ($0.22 \leq \lambda_{12}^0 \leq 0.25$). For the UNIFAC model the scaling factors were slightly different to those obtained with the van Laar and NRTL models; however, an inspection of the values of λ_{12}^0 determined at the same temperature shows that the differences between them are rather small. Therefore, it can be expected that the prediction of multicomponent vapor–liquid equilibria would be satisfactory if a mean value $\bar{\lambda}_i$ for the UNIFAC model is used.

3.2. Prediction of vapor–liquid equilibria at high pressures

Binary vapor–liquid equilibrium calculations were performed over a large range of temperatures and pressures using the activity coefficient parameters estimated at the reference temperature together with temperature-dependent scaling factors $\lambda_{12}(T)$ estimated through Eq. (15). For comparison, the same vapor–liquid equilibrium calculations were performed in a similar fashion as presented by Wong et al. [13]. In fact, the method used was that reported in a previous paper [12] by the same authors but using the PRSV [28] equation of state in conjunction with the van Laar model and scaling factors estimated by these authors.

The predictions of vapor–liquid equilibria obtained at high temperatures with our proposed approach and that of Wong et al. [13] are given in Table 3. Figs. 1–6 show the predictions

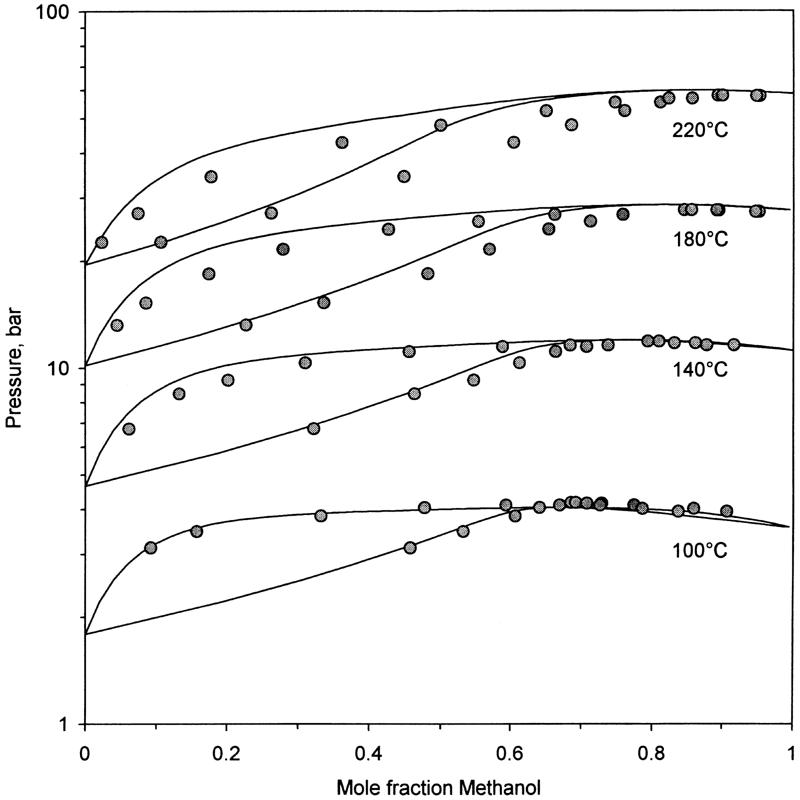

Fig. 1. Vapor–liquid equilibria for the methanol–benzene system using the translated PRCRP equation of state with the van Laar activity coefficient model. Points are experimental data of Butcher and Medani [57].

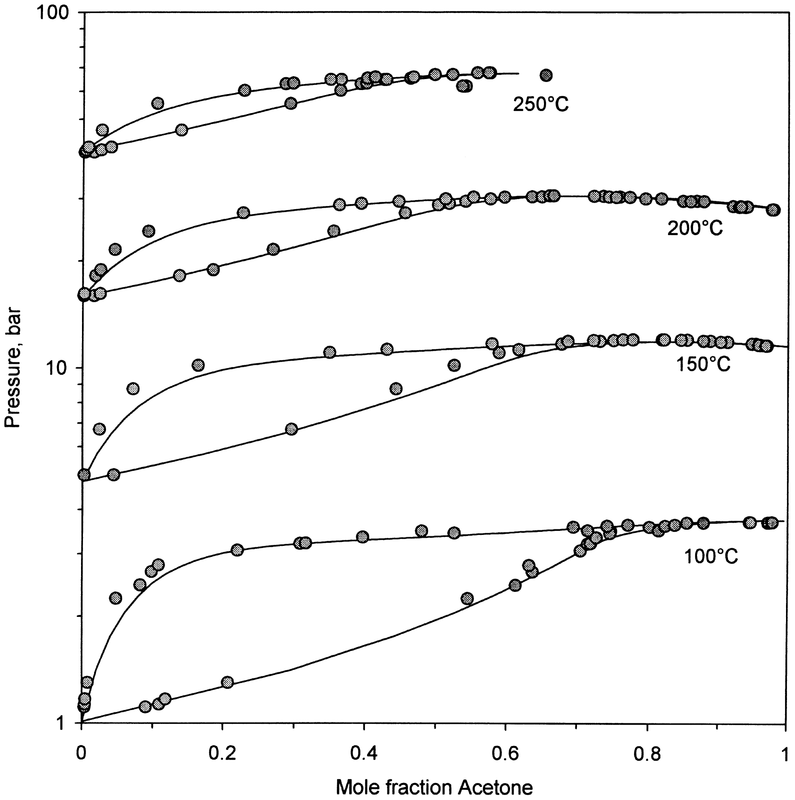

Fig. 2. Vapor–liquid equilibria for the acetone−water system using the translated PRCRP equation of state with the van Laar activity coefficient model. Points are experimental data of Griswold and Wong [58].

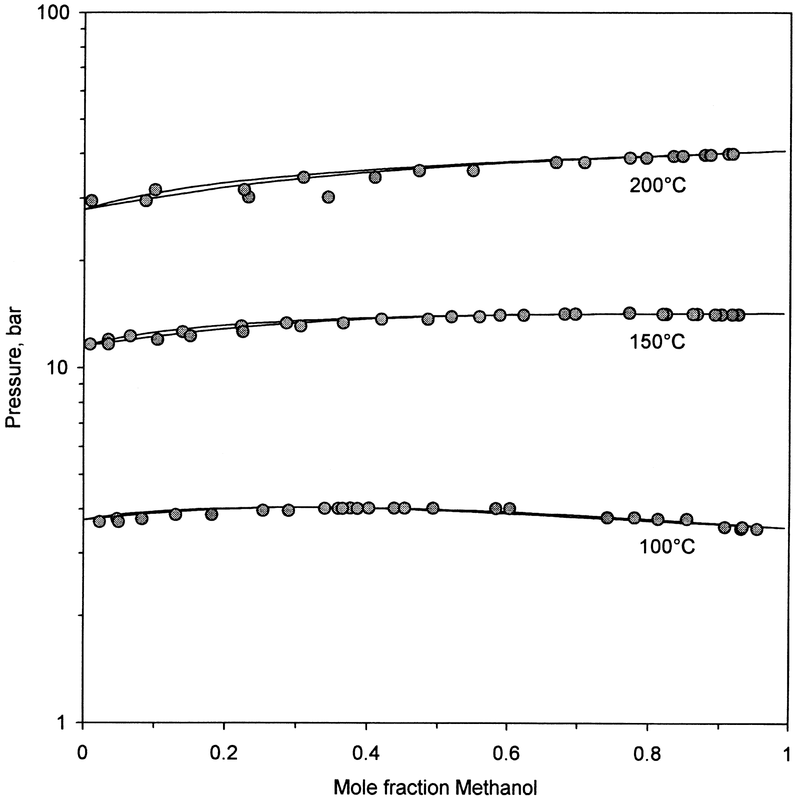

Fig. 3. Vapor–liquid equilibria for the methanol−acetone system using the translated PRCRP equation of state with the van Laar activity coefficient model. Points are experimental data of Griswold and Wong [58].

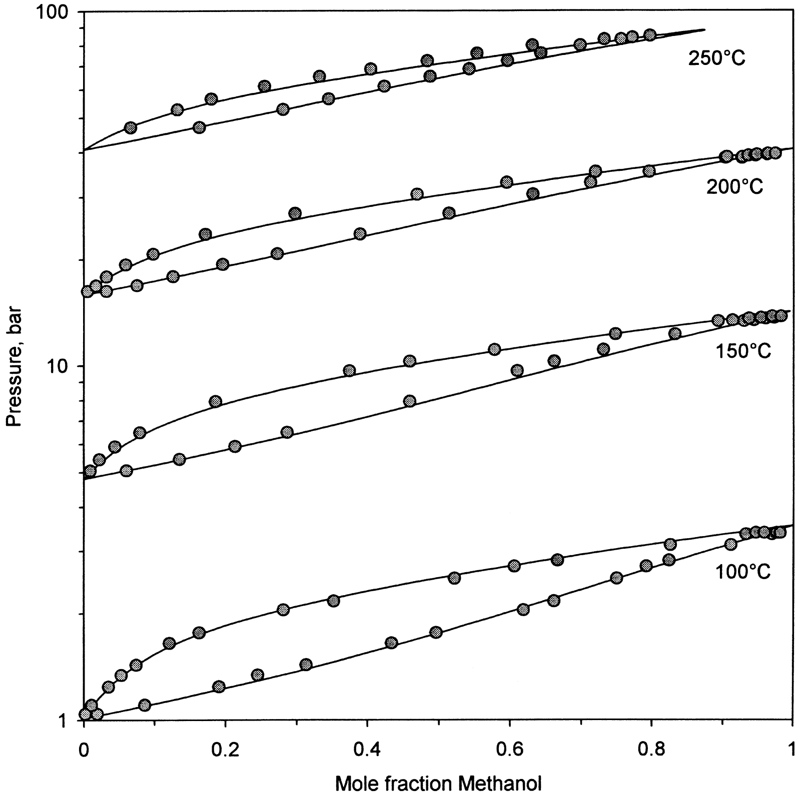

Fig. 4. Vapor–liquid equilibria for the methanol−water system using the translated PRCRP equation of state with the van Laar activity coefficient model. Points are experimental data of Griswold and Wong [58].

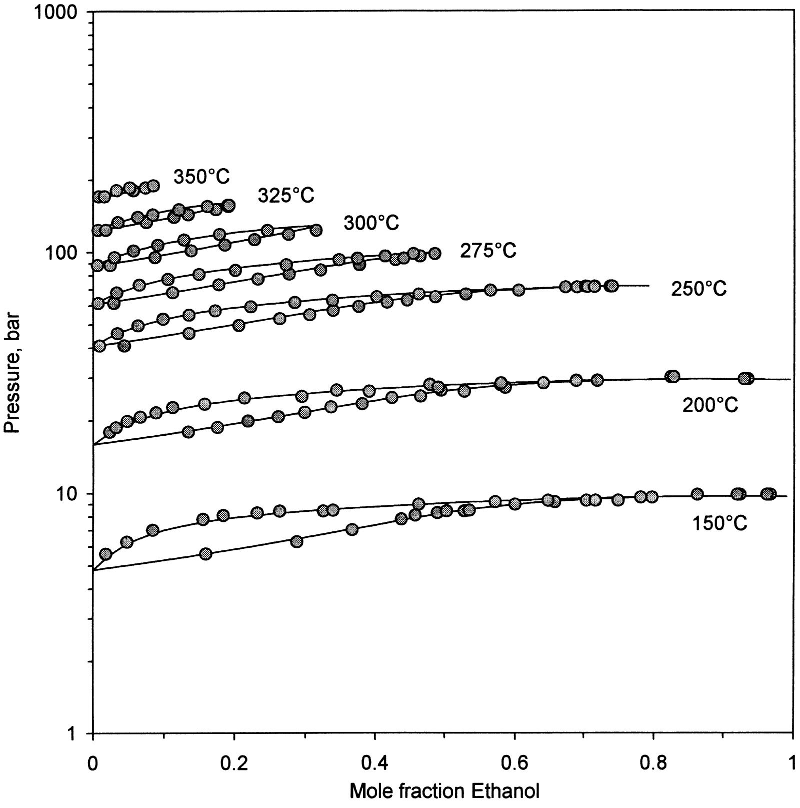

Fig. 5. Vapor–liquid equilibria for the ethanol−water system using the translated PRCRP equation of state and with van Laar activity coefficient model. Points are experimental data of Barr-David and Dodge [59].

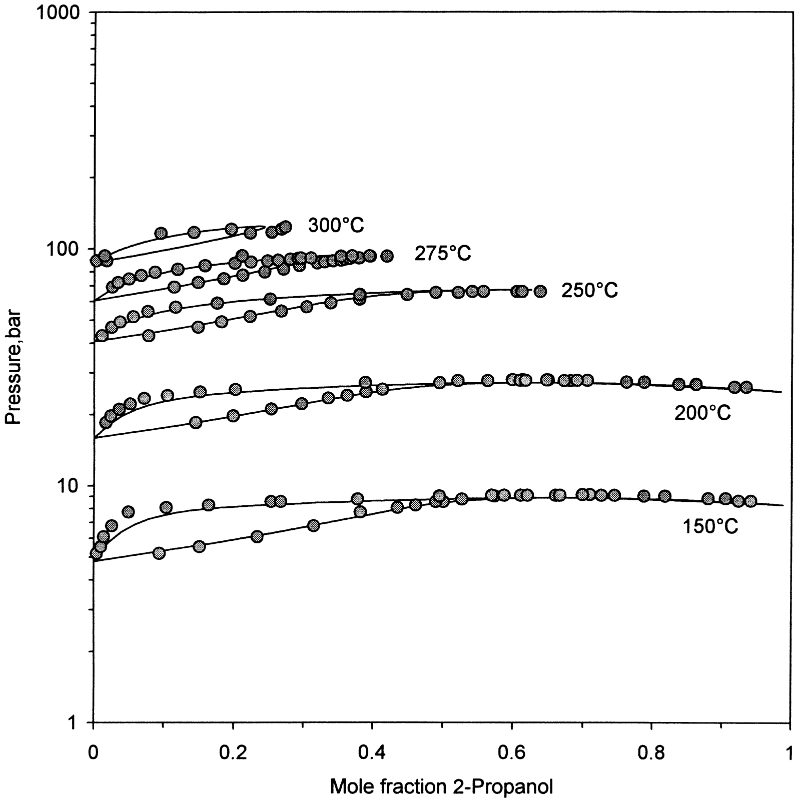

Fig. 6. Vapor–liquid equilibria for the 2-propanol–water system using the translated PRCRP equation of state with the van Laar activity coefficient model. Points are experimental data of Barr-David and Dodge [59].

obtained by us using the translated PRCRP equation of state associated with the van Laar activity coefficient model.

An inspection of Table 3 shows that the use of different excess free energy models using our approach does not affect the accuracy of the predictions. In general, very similar results were obtained for the systems studied using the van Laar, NRTL or UNIFAC model. Therefore, high-pressure vapor–liquid equilibrium predictions were equivalent regardless of the model chosen, even if some binary mixtures were better represented with a given model at the reference temperature as, for instance, the methanol–benzene or water–ethanol systems using the modified UNIFAC model (see Table 2).

Table 3 also shows that there is a rather poor agreement between experimental and calculated vapor–liquid equilibria for the methanol–benzene system [57] using our approach in comparison to that obtained with the Wong and Sandler [12] method. However, it is interesting to notice that Fig. 3 of Wong et al. [13] paper shows larger deviations at 373.15 K than those obtained at greater temperatures even if their scaling factors were estimated at this temperature. Unfortunately, these authors gave no explanation to this inconsistency. Conversely, as can be seen in Table 3 and Fig. 1, our method shows that in so far as the temperature increases, greater deviations are obtained; the overall relative deviation in pressure being about 5% for this system.

For the acetone–water, acetone–methanol, and methanol–water systems [58], with scaling factors estimated at 373.15 K, the results obtained with the two methods were comparable and very satisfactory even at high temperatures. Table 3 shows that the deviations between experimental and calculated pressures are in the range of 1–2%. Figs. 2–4 illustrate the predictions obtained with our method. For the ethanol–water and 2-propanol–water systems [59], however, a comparison between the two methods is less evident. That is, Wong et al. [13] used isobaric vapor–liquid equilibrium data for the estimation of their scaling factor while we considered only isothermal vapor–liquid equilibrium data for the estimation of our scaling factor. The overall relative deviations obtained with the Wong and Sandler method are about 2 and 3% in pressure (see Table 3) for the systems ethanol–water and 2-propanol–water, respectively, while those obtained with our method are about of 1 and 2%, which is quite satisfactory. Figs. 5 and 6 illustrate these results.

3.3. *Predictions of vapor–liquid equilibria at low and moderate pressures*

Table 4 presents the predictions of the vapor–liquid equilibria obtained at low and moderate pressures for the systems studied above by using the proposed and Wong–Sandler methods. This table shows that the results obtained using our

Table 4
Vapor–liquid equilibria deviations on pressure, $\delta P/P$, and on vapor mole fractions, δy, for binary mixtures at low and moderates pressures using the Wong–Sandler and the proposed methods

T (K)	N_p	Wong–Sandler		This work						Reference
		van Laar		van Laar		NRTL		UNIFAC		
		$\delta P/P$ (%)	δy	$\delta P/P$ (%)	δy	$\delta P/P$ (%)	δy	$\delta P/P$	δy	
Methanol−benzene										
288.15	11	9.00		2.38		2.41		2.84		[60]
298.15	28	10.22		5.09		5.07		5.24		[61]
298.15	9	9.79	0.040	3.55	0.019	3.51	0.020	4.10	0.021	[62]
298.15	11	8.77		2.75		2.73		2.99		[60]
308.15	8	6.57		2.66		2.66		2.64		[63]
308.15	9	10.41	0.059	4.65	0.023	4.60	0.024	4.89	0.029	[64]
308.15	11	8.42		2.92		2.90		2.99		[60]
311.65	7	8.51	0.037	3.46	0.010	3.39	0.010	4.16	0.011	[65]
313.15	14	6.95	0.052	3.11	0.027	3.14	0.026	2.71	0.033	[66]
313.15	15	6.16		2.69		2.72		2.35		[67]
318.15	11	8.00		2.92		2.90		2.84		[60]
328.15	5	14.34	0.080	4.83	0.025	4.59	0.024	6.45	0.034	[68]
328.15	9	10.17	0.058	4.61	0.022	4.56	0.022	4.64	0.025	[64]
328.15	11	7.55		2.83		2.86		2.57		[60]
363.15	6	5.97	0.026	1.63	0.020	1.79	0.021	0.92	0.015	[69]
373.15	12	4.47	0.022	2.04	0.012	2.19	0.012	0.70	0.070	[57]
Total	177	8.37	0.046	3.38	0.020	3.38	0.020	3.36	0.023	
Acetone−water										
288.15	13	10.57		12.31		11.97		10.62		[70]
298.15	13	8.57		10.36		9.85		9.92		[70]
303.15	5	6.73		5.35		4.97		4.21		[71]
308.15	5	6.87		3.98		3.62		2.74		[71]
308.15	13	7.06		6.97		6.67		6.77		[70]
308.15	21	6.03	0.018	4.66	0.015	4.34	0.015	5.32	0.012	[72]
318.15	13	5.78		4.32		4.06		4.18		[70]
323.15	17	3.83		2.35		2.10		1.79		[73]
373.15	22	2.80	0.007	3.27	0.014	3.37	0.014	4.22	0.019	[74]
Total	122	6.06	0.012	5.70	0.015	5.47	0.014	5.57	0.016	
Methanol−acetone										
288.15	10	1.75		3.40		3.25		2.63		[75]
298.15	10	1.54		1.13		0.97		1.69		[75]
298.15	14	3.33	0.038	5.08	0.052	5.01	0.050	4.96	0.043	[76]
308.15	10	0.98		1.22		1.09		2.22		[75]
318.15	10	0.85		1.97		1.85		1.62		[75]
323.15	4	1.73		3.40		3.35		3.15		[77]
323.15	28	2.03		3.99		3.90		3.51		[78]
328.15	10	3.09		1.76		1.74		0.83		[75]
Total	96	2.01	0.038	3.03	0.052	2.94	0.050	2.81	0.043	
Methanol−water										
298.15	8	2.91		4.80		5.16		4.79		[79]
298.15	10	1.17	0.005	2.90	0.009	3.30	0.011	3.64	0.006	[80]
308.15	13	1.07	0.009	1.66	0.013	1.79	0.015	1.71	0.010	[81]
313.15	10	0.94	0.005	0.78	0.006	0.83	0.006	0.88	0.002	[82]
313.15	15	3.24	0.013	5.20	0.019	6.03	0.022	4.94	0.019	[83]
313.15	10	2.24		3.07		3.41		3.61		[84]
322.91	13	2.99	0.020	3.60	0.024	3.95	0.024	3.62	0.018	[85]
323.15	8	1.55		1.86		2.00		1.65		[79]
323.15	13	1.00	0.010	1.62	0.014	1.74	0.016	0.77	0.009	[81]
333.15	12	1.38	0.012	2.23	0.017	2.36	0.017	0.67	0.008	[86]
333.15	7	1.61		1.76		1.52		0.85		[87]
338.15	12	0.82	0.006	1.22	0.009	1.21	0.009	0.70	0.004	[81]
373.15	16	1.36	0.009	1.40	0.010	1.42	0.010	2.54	0.009	[57]
413.15	6	1.96	0.009	1.69	0.012	1.45	0.011	1.10	0.008	[88]
Total	153	1.73	0.010	2.45	0.014	2.65	0.014	2.33	0.010	

Table 4 (*Continued*)

T (K)	N_p	Wong–Sandler		This work						Reference
		van Laar		van Laar		NRTL		UNIFAC		
		$\delta P/P$ (%)	δy	$\delta P/P$ (%)	δy	$\delta P/P$ (%)	δy	$\delta P/P$	δy	
Ethanol–water										
293.15	19	5.24		5.67		5.49		4.49		[89]
298.15	12	7.01	0.038	5.22	0.026	5.26	0.026	4.32	0.018	[90]
303.15	25	4.67	0.022	3.31	0.020	3.24	0.020	2.85	0.015	[91]
313.15	12	5.22	0.021	3.26	0.036	3.20	0.036	2.56	0.034	[92]
313.15	19	4.79		3.45		3.30		2.43		[89]
313.15	12	7.34	0.031	1.90	0.012	1.91	0.012	1.37	0.009	[93]
323.15	8	6.25		1.71		1.79		1.22		[79]
323.15	9	6.14	0.036	1.14	0.004	1.21	0.005	0.91	0.008	[94]
323.15	26	4.89	0.025	1.07	0.008	1.01	0.007	0.73	0.004	[91]
327.96	12	6.58	0.042	1.27	0.010	1.35	0.009	0.85	0.011	[95]
328.15	13	7.53	0.030	0.53	0.008	0.50	0.008	0.59	0.007	[93]
343.15	13	7.66	0.029	1.16	0.005	1.15	0.005	1.61	0.008	[93]
343.15	26	5.13	0.026	0.46	0.002	0.45	0.002	0.72	0.005	[91]
348.15	7	7.07	0.042	0.58	0.008	0.57	0.008	1.28	0.014	[94]
363.15	26	5.31	0.025	1.18	0.006	1.22	0.006	1.46	0.010	[91]
Total	239	5.74	0.028	2.16	0.011	2.13	0.011	1.86	0.011	
2-Propanol–water										
303.15	18	6.98	0.039	6.57	0.039	5.93	0.030	3.23	0.026	[96]
308.15	8	5.23	0.027	9.57	0.041	8.65	0.026	4.69	0.022	[97]
318.15	18	6.21	0.048	3.66	0.023	3.30	0.021	1.49	0.025	[96]
318.15	8	5.37	0.028	6.58	0.031	5.77	0.017	2.22	0.014	[97]
333.15	18	5.34	0.048	2.52	0.028	1.83	0.024	2.05	0.035	[96]
338.15	8	5.19	0.025	2.79	0.018	2.00	0.007	1.58	0.010	[97]
423.15	19	1.81	0.016	2.53	0.024	2.81	0.028	4.84	0.030	[59]
Total	97	5.10	0.034	4.42	0.029	3.96	0.024	2.91	0.025	

method are about of the same order of magnitude whichever the excess free energy model considered.

An examination of Table 4 shows that for the methanol–benzene system, the deviations between experimental and calculated pressures are about 3 and 8% with our method and that of Wong and Sandler, respectively. As expected, in accordance with the predictions at high temperatures, the results obtained at lower and moderates temperatures using our method were more satisfactory while with the Wong–Sandler method worse results were obtained in so far as the temperature decreases.

For the systems, acetone–methanol and methanol–water, good predictions were obtained with the two methods; however, smaller deviations from experimental pressures were obtained with the Wong–Sandler method. On the contrary, bad predictions of the vapor–liquid equilibria were obtained with both methods for the acetone–water system.

Table 5

Vapor–liquid equilibrium deviations on pressure, $\delta P/P$, and on vapor mole fractions, δy, using the modified translated PRCRP equation of state associated with activity coefficient models[a]

System	Temperature or pressure	N_p	Van Laar		NRTL		UNIFAC	
			$\delta P/P$ (%)	δy	$\delta P/P$ (%)	δy	$\delta P/P$ (%)	δy
Acetone–methanol–water	373.15 K	51	6.58	0.044	4.81	0.037	5.18	0.047
	523.15 K[b]	57	3.93	0.015	2.76	0.013	3.44	0.015
	1.013 bar	58	5.56	0.050	5.13	0.049	6.75	0.069
	1.013 bar	54	6.63	0.025	5.07	0.021	2.25	0.015
	Total	220	5.64	0.033	4.43	0.030	4.42	0.037

[a] Data taken from DECHEMA Chemistry Data Series [44].

[b] Taken from Griswold and Wong [58].

For the ethanol–water and 2-propanol–water systems, the deviations are in the range of about 1.9 and 3.5% in pressure with our method while with the Wong–Sandler method the deviations were of 5.6 and 5.1%, respectively.

On the basis of the results reported above, it could be said that the choice of the activity coefficient model (van Laar, NRTL or UNIFAC) does not significantly affect the prediction of the vapor–liquid equilibria for the systems studied. That is, the predictions obtained show that the proposed method and that of Wong and Sandler gave similar results at high pressures; however, it seems that more accurate predictions are obtained with the proposed method at low pressures.

3.4. Prediction of vapor–liquid equilibria for ternary systems

Vapor–liquid equilibria for the ternary system acetone–methanol–water at different temperatures and pressures are given in Table 5. The calculations were performed with the corresponding binary scaling factors λ_{ij} for the van Laar and NRTL models and with the mean values $\overline{\lambda}_i$ of each component for the UNIFAC model.

An inspection of this table shows that results obtained with the NRTL and UNIFAC models were more satisfactory than those obtained with the van Laar model. However, all ternary predictions could be considered satisfactory since the only necessary information required in these calculations were the reported activity coefficient parameters at the reference temperature and a scaling factor estimated at the same temperature.

4. Conclusions

A simple and thermodynamically consistent method to predict vapor–liquid equilibria in a large range of temperatures and pressures has been presented. The method is based on a similar principle as that developed by Wong and Sandler, which requires solely the activity coefficient parameters reported in the literature at a single temperature. Nonetheless, this method is more general in the sense that it can be applied to either cubic or non-cubic equations of state since the proposed method is based on the constant packing fraction reference. The proposed method, contrary to the Wong and Sandler method assures a linear mixing rule for co-volumes which simplifies its application in existing routines to calculate multi-component vapor–liquid equilibria.

In addition, a generalization of the van Laar activity coefficient model to be applied to multicomponent mixtures has been developed.

Finally, the results of vapor–liquid equilibria obtained with different activity coefficient models (van Laar, NRTL, and UNIFAC) show that our method gives similar and sometimes better predictions at low pressures than those obtained with the Wong–Sandler method.

5. Nomenclature

a	equation of state energy parameter
a_0	pure-component parameter $a(T)$, $T=T_b$
a_m	pure-component parameter $a(T)$, $T\leq T_b$
a_s	pure-component parameter $a(T)$, $T>T_b$
A	Helmholtz free energy of the mixture
$\underline{A}$	molar Helmholtz free energy
A^E	excess Helmholtz free energy
A^*	Helmholtz free energy at the ideal gas state
A_{ij}	binary interaction parameter of the van Laar activity coefficient
b	equation of state size parameter, co-volume
B	second virial coefficient
C_{ij}	binary coefficient parameter of the van Laar model
$E(T,\boldsymbol{x})$	residual excess function
E_{ij}	interaction parameter in the excess function formalism
$F(\eta)$	packing fraction function
g_{ij}	local composition factor for the NRTL model
G_{ij}	NRTL model parameter
k_{ii}	interaction parameter in the mixing rule
m_1, m_2	equation of state adjustable parameters for pure-component
m_s	parameter, Eq. (B.5)
N_p	number of experimental points
P	pressure
p	number of components
$Q(\eta)$	packing fraction function
$Q'(\eta)$	derivative of packing fraction function with respect to η
R	gas constant
T	temperature
T_b	normal boiling temperature point
v	molar volume
x_i	liquid mole fraction of component i
X	temperature-dependent parameter, Eq. (B.4)
y_i	vapor mole fraction of component i
z	compressibility factor
z_i	compressibility factor of component i
z^E	excess compressibility factor

Greek letters

α_{ij}^0	NRTL model binary parameter
β	parameter, Eq. (15)
δ_i	correlation parameter, $\delta_i=\sqrt{a}/b_i$
γ	factor characterizing a given cubic equation of state
γ_i	activity coefficient of component i
γ_i^C	combinatorial part of UNIFAC activity coefficient
γ_i^C	residual part of UNIFAC activity coefficient
η	constant packing fraction, $\eta=b/v$
γ_{ij}	binary scaling factor
λ_∞	limit scaling factor (infinite temperature)

τ_{ij}^{0}	NRTL model binary parameter
κ_0, κ_1	PRSV equation-of-state parameters
ω	acentric factor

Subscripts

c	critical property
i, j, k, l, m	component index
∞	infinite pressure or temperature state

Superscripts

calc	calculated property
exp	experimental property
E	excess property
0	property at the reference temperature T
*	referent to ideal state

Appendix A. Excess functions and reference to infinite pressure or constant packing fraction for cubic equations of state

The molar excess Helmholtz free energy for a mixture of p components derived from a cubic equation of state, at constant temperature and pressure, can be written as:

$$\begin{aligned}\underline{A}^{\mathrm{E}}(T,P,\boldsymbol{x}) = {} & -RT\ln\left[\frac{Pb(1-\eta)}{RT\eta}\right]-\frac{a}{b}Q(\eta)\\ & +RT\sum_{i=1}^{p}x_i\ln\left[\frac{Pb_i(1-\eta_i)}{RT\eta_i}\right]\\ & +\sum_{i=1}^{p}x_i\frac{a_i}{b_i}Q(\eta_i)\end{aligned}\tag{A.1}$$

where

$$Q(\eta)=\int_{\eta=0}^{\eta}Q'(\eta)\frac{\mathrm{d}\eta}{\eta}\tag{A.2}$$

with $Q(\eta)=\eta$ for the van der Waals equation and $Q(\eta)=\ln[(1+c_2\eta)/(1+c_1\eta)]/(c_2-c_1)$ for all other cubic equations of state (e.g. SRK and PR); c_1 and c_2 being two constants characterizing the specific equation of state.

For a given model of the excess free energy, A^{E}, the ratio a/b for a mixture with p components can, in turn, be written as:

$$\begin{aligned}\frac{a}{b}=\frac{1}{Q(\eta)}\Bigg\{ & RT\sum_{i=1}^{p}x_i\ln\left[\frac{Pb_i(1-\eta_i)}{RT\eta_i}\right]+\sum_{i=1}^{p}x_i\frac{a_i}{b_i}Q(\eta_i)\\ & -RT\ln\left[\frac{Pb(1-\eta)}{RT\eta}\right]-\underline{A}^{\mathrm{E}}(T,P,\boldsymbol{x})\Bigg\}\end{aligned}\tag{A.3}$$

which must be independent of η to be introduced in the equation of state.

If the infinite pressure reference (see [1]) is introduced into Eq. (A.3), it can be rewritten as

$$\frac{a}{b}=\sum_{i=1}^{p}x_i\frac{a_i}{b_i}-\frac{\underline{A}^{\mathrm{E}}_{\infty}(T,\boldsymbol{x})}{\lambda_{\infty}}\tag{A.4}$$

where λ_{∞} is the limit value of the scaling factor as the temperature goes to infinite and it is equal to $Q(\eta=1)$ given in Eq. (A.2). For the Peng–Robinson equation of state, $\lambda_{\infty}=-(1/\sqrt{2})\ln(\sqrt{2}-1)$, while for translated Peng–Robinson [40] equation of state, $\lambda_{\infty}=-(1/c_2)\ln(1+c_1)$ with $c_2=2+2\sqrt{2}$.

If the packing fraction η of the mixture at given temperature and pressure is assumed to satisfy the relation

$$\eta=\frac{b}{v}=\eta_i=\frac{b_i}{v_i}\tag{A.5}$$

where v_i is the molar volume of component, i, evaluated at temperature T and under a pressure leading to the constant packing fraction of the mixture, and if the excess Helmholtz energy is assumed to be the sum of the athermal term of the Flory-type model [30] and of the residual term $\underline{A}^{\mathrm{E}}_{\mathrm{res}}=E(T,\boldsymbol{x})Q(\eta)$, then Eq. (A.3) can be expressed as

$$\frac{a}{b}=\sum_{i=1}^{p}x_i\frac{a_i}{b_i}-E(T,\boldsymbol{x})\tag{A.6}$$

which is equivalent to Eq. (A.4) by using the following relation

$$E(T,\boldsymbol{x})=\frac{\underline{A}^{\mathrm{E}}_{\infty}(T,\boldsymbol{x})}{\lambda_{\infty}}\tag{A.7}$$

Thus, we have shown that for equations of state, the reference states at infinite pressure or constant packing fraction, η, are equivalent.

Appendix B. The translated PRCRP equation of state

The translated PRCRP equation of state [40] was established through Eqs. (6)–(9) in conjunction with constants $c_1=0$ and $c_2=2+2\sqrt{2}$. For pure components, parameters a and b are estimated as:

$$a=\begin{cases}a_{\mathrm{m}} & \text{if } T\le T_{\mathrm{b}}\\ a_{\mathrm{s}} & \text{if } T\ge 1.25T_{\mathrm{b}}\\ Xa_{\mathrm{s}}+(1-X)a_{\mathrm{m}} & \text{if } T_{\mathrm{b}}\le T\le 1.25T_{\mathrm{b}}\end{cases}\tag{B.1}$$

where

$$a_{\mathrm{m}}=a_0\left\{1+m_1\left[1-\left(\frac{T}{T_{\mathrm{b}}}\right)^{1/2}\right]-m_2\left(1-\frac{T}{T_{\mathrm{b}}}\right)\right\}\tag{B.2}$$

$$a_{\mathrm{s}}=a_{\mathrm{c}}\left\{1+m_0\left[1-\left(\frac{T}{T_{\mathrm{c}}}\right)^{1/2}\right]\right\}^2\tag{B.3}$$

and

$$X=\frac{(T-T_{\mathrm{b}})^2}{(T-T_{\mathrm{b}})^2+(1.25T_{\mathrm{b}}-T)^2}\tag{B.4}$$

where a_0 is the value of parameter $a(T)$ estimated at the normal boiling temperature T_b, and parameters a_c, b, and m_0 are, in turn, estimated from the critical properties and normal boiling temperature of pure components, i.e.

$$a_c = 0.45724 \frac{R^2 T_c^2}{P_c} \tag{B.5}$$

$$m_0 = \frac{(a_0/a_c)^{1/2} - 1}{1 - (T_b/T_c)^{1/2}} \tag{B.6}$$

$$b = 0.045572 \frac{RT_c}{P_c} \tag{B.7}$$

References

[1] M.-J. Huron, J. Vidal, Fluid Phase Equilibria 3 (1979) 255.
[2] J. Mollerup, Fluid Phase Equilibria 25 (1986) 323.
[3] P.A. Gupte, T.E. Daubert, Fluid Phase Equilibria 28 (1986) 155.
[4] R. Gani, N. Tzouvaras, P. Rasmussen, A. Fredenslund, Fluid Phase Equilibria 47 (1989) 133.
[5] S. Dahl, M.L. Michelsen, AIChE J. 36 (1990) 1829.
[6] M.L. Michelsen, Fluid Phase Equilibria 60 (1990) 47.
[7] M.L. Michelsen, Fluid Phase Equilibria 60 (1990) 213.
[8] R. Heidemann, S.L. Kokal, Fluid Phase Equilibria 56 (1990) 17.
[9] T. Holderbaum, J. Gmehling, Fluid Phase Equilibria 70 (1991) 251.
[10] S. Dahl, A. Fredenslund, P. Rasmussen, Ind. Eng. Chem. Res. 30 (1991) 1936.
[11] C. Lermite, J. Vidal, Fluid Phase Equilibria 72 (1992) 111.
[12] D.S.H. Wong, S.I. Sandler, AIChE J. 38 (1992) 671.
[13] D.S.H. Wong, H. Orbey, S.I. Sandler, Ind. Eng. Chem. Res. 31 (1992) 2033.
[14] H. Huang, S.I. Sandler, Ind. Eng. Chem. Res. 32 (1993) 1498.
[15] H. Orbey, D.S.H. Wong, S.I. Sandler, Fluid Phase Equilibria 85 (1993) 41.
[16] C. Boukouvalas, N. Spiliotis, P. Coutsikos, N. Tzouvaras, D. Tassios, Fluid Phase Equilibria 92 (1994) 74.
[17] K. Tochigi, P. Kolár, T. Iisumi, K. Kojima, Fluid Phase Equilibria 96 (1994) 215.
[18] H. Orbey, S.I. Sandler, Fluid Phase Equilibria 111 (1995) 53.
[19] K. Fisher, J. Gmehling, Fluid Phase Equilibria 112 (1995) 1.
[20] C.R. Novenario, J.M. Caruthers, K.-C. Chao, Ind. Eng. Chem. Res. 35 (1996) 269.
[21] M.L. Michelsen, R.A. Heidemann, Ind. Eng. Chem. Res. 35 (1996) 278.
[22] K. Fisher, J. Gmehling, Fluid Phase Equilibria 121 (1996) 185.
[23] H. Orbey, S.I. Sandler, Fluid Phase Equilibria 132 (1997) 1.
[24] A. Fredenslund, J. Gmehling, P. Rasmussen, Vapor–Liquid Equilibria Using UNIFAC, Elsevier, New York, 1977.
[25] G. Soave, Chem. Eng. Sci. 27 (1972) 1197.
[26] H. Renon, J.M. Prausnitz, AIChE J. 14 (1968) 135.
[27] D.-Y. Peng, D.B. Robinson, Ind. Eng. Chem. Fundam. 15 (1976) 59.
[28] R. Stryjek, J.H. Vera, Can. J. Chem. Eng. 64 (1986) 323.
[29] G. Wilczek-Vera, J.H. Vera, Fluid Phase Equilibria 51 (1989) 197.
[30] A. Péneloux, W. Abdoul, E. Rauzy, Fluid Phase Equilibria 47 (1989) 115.
[31] J. Gmehling, J. Li, M. Schiller, Ind. Eng. Chem. Res. 32 (1993) 178.
[32] E. Rauzy, A. Péneloux, Int. J. Thermophys. 7 (1986) 635.
[33] B. Angus, B. Armstrong, K.M. de Reuck, Carbon Dioxide International Thermodynamic Tables of the Fluid State, IUPAC Commission on Thermodynamics and Thermochemistry, Pergamon Press, London, 1976.
[34] R. Solimando, E. Neau, A. Péneloux, M. Rogalski, Rev. Inst. Franç. Pét. 50 (1995) 791.
[35] C.H. Chien, R.A. Greenkorn, K.-C. Chao, AIChE J. 29 (1983) 560.
[36] C. Lermite, J. Vidal, Fluid Phase Equilibria 42 (1988) 1.
[37] E. Behar, R. Simonet, E. Rauzy, Fluid Phase Equilibria 21 (1985) 237.
[38] R. Solimando, M. Rogalski, E. Neau, A. Péneloux, Fluid Phase Equilibria 82 (1993) 369.
[39] O. Redlich, J.N.S. Kwong, Chem. Rev. 44 (1949) 233.
[40] E. Rauzy, Ph.D. Dissertation, Université d'Aix Marseille II, Marseille, 1982.
[41] B. Carrier, M. Rogalski, A. Péneloux, Ind. Eng. Chem. Res. 27 (1988) 1714.
[42] J. Gmehling, U. Onken, Vapor–liquid equilibrium data collection, in: Aqueous Organic Systems, Chemistry Data Series, Vol. 1, Part 1, DECHEMA Publication, Frankfurt/Main, Germany, 1977.
[43] J. Gmehling, U. Onken, Vapor–liquid equilibrium data collection, in: Organic Hydroxy Compounds: Alcohols, Chemistry Data Series, Vol. 1, Part 2a, DECHEMA Publication, Frankfurt/Main, Germany, 1977.
[44] J. Gmehling, U. Onken, W. Artl, Vapor–liquid equilibrium data collection, in: Aqueous Organic Systems, Chemistry Data Series, Vol. 1, Part 1a, DECHEMA Publications, Frankfurt/Main, Germany, 1981.
[45] C.J. Willingham, W.J. Taylor, J.M. Pignocco, F.D. Rossini, J. Res. Natl. Bur. Standards 35 (1945) 219.
[46] D. Ambrose, J. Chem. Thermodyn. 13 (1981) 1161.
[47] I. Brown, F. Smith, Aust. J. Chem. 10 (1957) 423.
[48] T. Boublik, K. Aim, V. Fried, E. Hala, The Vapor Pressures of Pure Substances, Elsevier, Amsterdam, 1975.
[49] D. Ambrose, C.H.S. Sprake, J. Chem. Thermodyn. 2 (1970) 631.
[50] T. Boublik, K. Aim, Coll. Czech. Chem. Commun. 37 (1972) 3513.
[51] H.F. Gibbard, J.L. Creek, J. Chem. Eng. Data 19 (1974) 308.
[52] Thermodynamic research center, thermodynamic tables, in: Vapor Pressure, The Texas A&M University System, College Station, TX, 1988.
[53] C.B. Kretschmer, R.J. Wiebe, J. Am. Chem. Soc. 71 (1949) 1793.
[54] J. Singh, G.C. Benson, Can. J. Chem. 46 (1968) 1249.
[55] O.R. Foz, J. Morcilio, A. Pérez-Macia A. Méndez, An. Real Soc. Españ. Fís. Quím. 508 (1955) 23.
[56] N.B. Vargaftik, Tables on the Thermophysical Properties of Liquids and Gases, 2nd Edition, Wiley, New York, 1975.
[57] K.L. Butcher, M.S. Medani, J. Appl. Chem. 18 (1968) 100.
[58] J. Griswold, S.Y. Wong, Chem Eng. Symp. Ser. 48 (1952) 18.
[59] F. Barr-David, B.F. Dodge, J. Chem. Eng. Data 4 (1959) 107.
[60] B. Goetschel, Wiss. Z. Univ. Rostock. Math. Naturwiss. Reihe. 18 (1969) 927.
[61] S.C. Hwang, R.L. Robinson, J. Chem. Eng. Data 22 (1977) 319.
[62] A. Iguchi, Kagaku Sochi 20 (1978) 66.
[63] M. Feller, J. McDonald, Anal. Chem. 22 (1950) 338.
[64] G. Scatchard, S.E. Wood, J.M. Mochel, J. Am. Chem. Soc. 68 (1946) 1957.
[65] A.G. Morachevsky, E.G. Komarova, Vestn. Leningrad. Univ. 12, Ser. Fiz. Khim. 1 (1957) 118.
[66] S.C. Lee, J. Phys. Chem. 35 (1931) 3558.
[67] P. Oracz, G. Kolasinska, B. Janaszewski, Unpublished Data, Department of Chemistry, Warsaw University.
[68] G. Scatchard, L.B. Ticknor, J. Am. Chem. Soc. 74 (1952) 3724.
[69] W. Jost, H. Roeck, W. Schroeder, L. Sieg, H.G. Wagner, Z. Phys. Chem. (Frankfurt) 10 (1957) 133.
[70] J.M. Rhim, S.S. Park, H.O. Lee, Hwahak Konghak 12 (1974) 179.
[71] S.G. D'Avila, M.L. Cotrim, Rev. Bras. Technol. 4 (1973) 191.
[72] I. Lieberwirth, H. Schuberth, Z. Phys. Chem. (Leipzig) 260 (1979) 669.
[73] M.M. Chaudhry, H.C. Van Ness, M.M. Abbott, J. Chem. Eng. Data 25 (1980) 254.
[74] R.C. Ernst, E.E. Litkenhous, J.W. Spanyer, J. Phys. Chem. 36 (1932) 842.
[75] J.M. Rhim, S.S. Park, Hwahak Konghak 13 (1975) 147.

[76] A. Tamir, A. Appelblat, M. Wagner, Fluid Phase Equilibria 6 (1981) 113.
[77] M.M. Abbott, J.K. Floess, G.E. Walsh, H.C. Van Ness, AIChE J. 21 (1975) 72.
[78] M.M. Abbott, H.C. Van Ness, AIChE J. 21 (1975) 62.
[79] K.A. Dulitskaya, Zh. Obshch. Khim. 15 (1945) 9.
[80] D.J. Hall, C.J. Mash, R.C. Pemberton, Report Chemistry, National Physical Laboratory, London, 1979.
[81] M.L. McGlashan, A.G. Williamson, J. Chem. Eng. Data 21 (1976) 196.
[82] G.A. Ratcliff, K.C. Chao, Can. J. Chem. Eng. 47 (1969) 148.
[83] J.B. Ferguson, W.S. Funnell, J. Phys. Chem. 33 (1929) 1.
[84] M. Ewert, Bull. Soc. Chim. Belg. 45 (1936) 493.
[85] G. Bredig, R. Bayer, Z. Phys. Chem. 130 (1927) 1.
[86] M. Broul, K. Hlavaty, J. Linek, Coll. Czech. Chem. Commun. 34 (1969) 3428.
[87] H. Schubert, Z. Phys. Chem. (Leipzig) 255 (1974) 165.
[88] W. Schroeder, Chem. Ing. Technol. 30 (1958) 523.
[89] V.G. Garbarenko, V.N. Stabnikov, Izv. Vyssh. Uchebn. Zaved. Pishch. Tekhnol. 4 (1960) 112.
[90] H.J.E. Dobson, J. Chem. Soc. 127 (1925) 2866.
[91] R.C. Pemberton, C.J. Mash, J. Chem. Thermodyn. 10 (1978) 867.
[92] V.V. Udovenko, L.G. Fatkulina, Zh. Fiz. Khim. 26 (1952) 1438.
[93] I. Mertl, Collect. Czech. Chem. Commun. 37 (1972) 366.
[94] A.V. Nikolskaya, Zh. Fiz. Khim. 20 (1946) 421.
[95] M.S. Vrevskii, Z. Phys. Chem. 81 (1913) 1.
[96] V.V. Udovenko, T.F. Mazanko, Zh. Fiz. Khim. 41 (1967) 1615.
[97] E. Sada, T. Morisue, J. Chem. Eng. Jpn. 8 (1975) 191.