A COMPARATIVE STUDY OF NUMERICAL METHODS FOR CALCULATING PHASE EQUILIBRIA IN FLUID MIXTURES FROM AN EQUATION OF STATE

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Abstract—Accurate numerical methods are needed to determine phase equilibria in fluid mixtures for industrial applications, especially when mixtures exhibit critical points. In this paper we test the reliability and consistency of predictions of three major approaches for computing vapor–liquid-phase equilibria in binary fluid mixtures based on the Soave–Redlich–Kwong equation of state and van der Waals one-fluid mixing rules. These approaches are fugacity method, Gibbs minimization method and area method. To examine the accuracy of the three methods, calculated results for the vapor–liquid-phase equilibria in two selected binary mixtures, namely, carbon dioxide/butane and carbon dioxide/propane, are compared with experimental data over a range of high temperatures (278–398 K) and elevated pressures (0.3–7 MPa). It has been found that the area method, which provides both necessary and sufficient conditions for Gibbs energy minimization of the entire system, is more reliable than either the fugacity method or Gibbs minimization method in determining the vapor–liquid-phase equilibria, especially close to the critical loci of the mixtures. The Gibbs minimization performs better than the fugacity method in locating phase equilibria in the vicinity of the critical locus of the mixtures. Far away from the critical loci of the mixtures all the three methods are found to be equally reliable. The area-method-based calculations illustrate that the SRK EOS/VDW MR model can predict reasonably well the vapor–liquid-phase equilibria in these binary mixtures. However, the SRK EOS/VDW MR model, which contains only a single binary interaction parameter, is unable to describe accurately the pressure dependence of the vapor- and the liquid-phase compositions. Copyright © 1996 Elsevier Science Ltd.

1. INTRODUCTION

The accurate prediction of phase equilibria of fluid mixtures is needed in many industrial applications, such as, reservoir modeling, process design, and gas processing and separation. In recent years, supercritical fluid extraction has been a viable alternative to conventional heavy hydrocarbon separation processes for petroleum refining industries (Stahl *et al.*, 1988). In the development of supercritical fluid extraction processes, the understanding of the relevant phase equilibrium over a wide range of temperatures and pressures, especially in the vicinity of critical points of the mixtures, is of fundamental importance (Brennecke and Eckert, 1989). The cubic equation of state (EOS) approach has been well suited for industrial calculations because of its mathematical simplicity, and also because simple numerical methods can be used to solve these equations which satisfy the phase equilibrium conditions. One of the most extensively used equations of state for modeling of fluid mixtures is the Soave–Redlich–Kwong (SRK) (Soave, 1972) EOS.

The major problems associated with the calculation of phase equilibria are that (1) the number of phases is not known in advance, and (2) close to the critical

locus of the mixture, calculation strongly depends on the initial values of the unknown variables (for instance, in a pressure–temperature-flash calculation the unknown variables are compositions of the phases) and the numerical method used, leading often to trivial solution with equilibrium phases having identical compositions.

In the equation of state (EOS) method, a single equation is used to represent thermodynamic properties of all the phases in pure fluids as well as in mixtures. In mixtures, mixing rules are required to determine the mixture parameters of the EOS. For this sake, simple van der Waals (VDW) one-fluid mixing rules (MR) have been very popular. For a well-defined EOS with adequate mixing rules, phase equilibria are usually determined by satisfying the equilibrium conditions of thermal stability, mechanical stability and material stability (Rowlinson and Swinton, 1982). The thermal stability demands that temperatures of the phases should be equal. Likewise, in the mechanical stability pressures of the phases should be the same. In the material stability, chemical potentials of each component in the phases should be the same. The material stability can be expressed in terms of the molar Gibbs energy of the mixtures (Sadus, 1992). For example, let us consider a binary mixture. For two phases [say, liquid (L) and vapor (V)] to be in equilibrium the chemical potentials for component 1 (or 2) in both phases should be

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equal, i.e.,

$$\mu_1^L = \mu_1^V \quad (\text{or } \mu_2^L = \mu_2^V) \qquad (1)$$

which leads to

$$G_m^L - G_m^V + (X_1^V - X_1^L)\left(\frac{\partial G_m}{\partial X_1}\right)_{T,P} = 0 \qquad (2)$$

where X_1 is the composition of component 1. According to eq. (2), in a phase equilibrium calculation the Gibbs energy of mixing should be minimum globally. That means, for the given temperature and pressure, a global minimum of the Gibbs energy function describes the true equilibrium values of the liquid- and vapor-phase compositions.

However, due to the presence of multiple local minima and the complexity of the models employed, most of the numerical approaches do not provide a guarantee of obtaining the global solution for several equilibrium problems. In recent years, the difficulty of finding the true equilibrium solution has stimulated much interest in developing efficient and accurate computational methods to minimize the Gibbs energy of mixing globally (McDonald and Floudas, 1995a–c; Eubank and Hall, 1995). In this paper we consider three approaches for calculating the vapor–liquid-phase equilibria in binary fluid mixtures consisting of carbon dioxide (CO_2) and hydrocarbons as examples. For such mixtures, accurate experimental data are available at high temperatures and elevated pressures. For example, extensive and accurate data exist for mixtures of CO_2–butane and CO_2–propane, ranging from subcritical to supercritical conditions of the mixtures. At the supercritical temperature of CO_2 and high pressures, these mixtures are seen to exhibit critical loci. Moreover, in separation processing and other applications it is often possible to lump multicomponents into pseudo-binaries.

The first method we consider is based on equating the fugacities (or chemical potentials) of each component of the two phases at given temperature and pressure and is called *fugacity method*. Although, in this method the material balance criteria are satisfied, in some cases the method fails to predict the correct number of phases or leads to trivial solutions. This may be due to the fact that the equality of the chemical potentials is a necessary but not a sufficient condition for minimizing the Gibbs energy of mixing of the entire system, as has been pointed out by Null (1970). In particular, in the critical region of the mixture, the solution is highly dependent on the initial values of the compositions (Baker *et al.*, 1982; Risnes and Dalen, 1984). In addition, the numerical techniques used to solve simultaneously the nonlinear equations may lead to a local minimum rather than to the global minimum of the Gibbs energy (Ammar and Renon, 1987).

The second method minimizes the Gibbs energy with respect to the mole numbers or compositions of the different components of the mixture (Trangenstein, 1985) at the given temperature and pressure. This method, referred to as the *Gibbs minimization method*, has been exploited by several workers (Michelsen 1982, 1994; Eubank and Barrufet, 1988; Cairns and Furzer, 1990). Since the optimization of the compositions depends on the derivatives of the Gibbs energy and the numerical tools for its minimization, even this method may not lead to the global minima in some cases. Rather, it can give solutions of the compositions corresponding to local minima or local maxima (Trangenstein, 1985). Moreover, if the initial values for the compositions are far away from the equilibrium compositions, this method can fail in describing phase instability and thus the phase equilibria in the mixtures (Swank and Mullins, 1986).

The third method we consider is a recent one, called the *area method*. This method provides both the necessary and the sufficient conditions for Gibbs energy minimization of the entire system (Eubank *et al.*, 1992). In this approach, two compositions in the region of the mixture are found such that the difference between the absolute area under the straight line connecting these two compositions and the absolute area of the Gibbs energy curve integrated between these same compositions should be at maximum and positive. For the area to be positive and maximum, the two compositions represent the equilibrium compositions for the mixture. When the area is negative in the entire composition range, there exists only a single phase. Furthermore, *area method* integrates the Gibbs energy curve to provide a maximum area rather than its derivative and is stable. It allows an accurate and efficient prediction of phase equilibria even close to the critical locus of a mixture where most of the iterative methods become unreliable. In their study, Eubank *et al.* (1992) tested the accuracy of the *area method* to a very few binary mixtures and a ternary mixture at selected conditions.

Recently, some more global optimization methods have been proposed by McDonald and Floudas (1995a–c) and by Eubank and Hall (1995). The former method is based on the Gibbs free energy of the activity coefficient models and the tangent plane stability criterion. The latter method is based on the Maxwell equal area rule. These methods are not considered here.

The purpose of the present paper is to make a systematic study of the above three methods for calculating the vapor–liquid-phase equilibria of a class of binary fluid mixtures using the simple Soave–Redlich–Kwong (SRK) EOS (Soave, 1972) and the van der Waals one-fluid mixing rules (VDW MR). We assess the relative performances of these numerical approaches by comparing calculated results with experimental data for CO_2–hydrocarbon mixtures as examples. Since our future goal is to apply a reliable method to model phase equilibria of reservoir fluids in supercritical conditions, particular emphasis will be given on calculating phase equilibria at high temperatures and elevated pressures, especially close to the

critical locus of the mixtures, and on testing the accuracy of the SRK EOS/VDW MR model.

In the next section we present theoretical background. This is followed by the presentation of *fugacity method*, *Gibbs minimization method* and *area method* in Section 3. In Section 4, we present comparisons of calculated results with experimental data for the vapor–liquid-phase equilibria of some selected binary systems. Finally, concluding remarks on the applications of these three methods are presented in Section 5.

2. EQUATION OF STATE AND MIXING RULES

For determining vapor–liquid-phase equilibria using an equation of state approach, the EOS must be able to describe both the vapor-phase and the liquid-phase behavior reliably. Van der Waals was the first to propose a simple cubic EOS, which accounts for the effects of both the repulsive and attractive forces in fluids (Rowlinson, 1988). However, the van der Waals EOS was able to represent thermodynamic properties of the fluids only qualitatively. Since then several more accurate cubic EOS have been developed for industrial calculations. One of the examples is the Redlich–Kwong (RK) EOS (Redlich and Kwong, 1949) which contains only two parameters. It was found that the RK EOS has a limited accuracy and is generally successful only for nearly ideal systems. To overcome these deficiencies, many modifications of the RK EOS have been proposed over the years. Important among them is the modification of the RK EOS due to Soave (1972), called Soave–Redlich–Kwong (SRK) EOS. SRK EOS has been widely used in calculating phase equilibria in fluids and fluid mixtures (Gibbons, 1984). In this paper, we adopt the SRK EOS, which contains only two parameters to describe properties of the pure fluids.

We consider a binary fluid mixture consisting of components 1 and 2. Thermodynamic properties of the mixture are described by the following SRK EOS (Soave, 1972):

$$P = RT/(V_m - b_m) - a_m/[V_m(V_m + b_m)] \quad (3)$$

where P, T, V_m and R are pressure, absolute temperature, mixture molar volume and gas constant, respectively. To extend the SRK EOS to mixtures, mixing rules must be introduced to calculate the values of the SRK energy parameter a_m and the covolume parameter b_m. In this work, a_m and b_m are given by the simple VDW MR,

$$a_m = \sum_i \sum_j X_i X_j a_{ij} \quad (4)$$

and

$$b_m = \sum_i X_i b_i \quad (5)$$

with

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \quad (6)$$

where the pure component parameters of the SRK EOS are given by

$$a_i = 0.42747\alpha_i R^2 T_{ci}^2/P_{ci} \quad (7)$$

$$b_i = 0.08664 R T_{ci}/P_{ci} \quad (8)$$

$$\alpha_i = [1 + m_i(1 - T_{ri}^{0.5})]^2 \quad (9)$$

and

$$m_i = 0.48 + 1.574\omega_i - 0.176\omega_i^2. \quad (10)$$

T_{ci}, P_{ci} and ω_i are critical temperature, critical pressure and acentric factor of the pure component i, respectively, and $T_{ri} = T/T_{ci}$. Parameters a_i and b_i are determined from the critical properties of the pure fluids. k_{ij} is a binary interaction parameter characteristic of each binary pair. Introduction of k_{ij} parameter in eq. (6) enhances the performance of the SRK EOS. SRK EOS with the VDW MR is known to describe thermodynamic properties of the simple binary fluid mixtures adequately (Anderko, 1990).

3. METHODS FOR CALCULATING THE PHASE EQUILIBRIUM

3.1. *Fugacity method (FM)*

FM is based on the equality of chemical potentials at fixed temperature and pressure. In this approach, the phase equilibrium condition requires that

$$[F_1^L]_{T,P} = [F_1^V]_{T,P} \quad (11)$$

and

$$[F_2^L]_{T,P} = [F_2^V]_{T,P} \quad (12)$$

where the fugacity coefficient F_i of ith component in a mixture using SRK EOS is given by (Soave, 1972)

$$\ln(F_i/PX_i) = (b_i/b_m)(PV_m/RT - 1)$$
$$- \ln[(P/RT)(V_m - b_m)]$$
$$- (a_m/RTb_m)\ln(1 + b_m/V_m)$$
$$\times \left[\left(2\sum_{j=1}^2 X_j a_{ij}/a_m\right) - (b_i/b_m)\right] \quad (13)$$

Equations (11)–(13) suggest that eqs (11) and (12) are functions of the temperature, pressure and composition of the vapor phase ($Y_1 = 1 - Y_2$) and that of the liquid phase ($X_1 = 1 - X_2$). For the well-defined binary parameters at the selected temperature and pressure, eqs (11) and (12) contain only two unknowns: compositions of the vapor and liquid phases. These compositions X_1 and Y_1 are obtained by solving eqs (11) and (12) simultaneously at the given temperature and pressure using a modified Levenberg–Marquardt algorithm (IMSL supplied subroutine, 1989). Densities of the vapor and the liquid phases are calculated numerically using the following equation:

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \quad (14)$$

where Z is the compressibility factor

$$Z = PV_m/RT$$

and the parameters A and B are defined as

$$A = a_mP/R^2T^2 \quad \text{and} \quad B = b_mP/RT. \quad (15)$$

The Newton–Raphson numerical technique has been used to determine the roots of eq. (14) in order to calculate the vapor and liquid densities (Eubank and Barrufet, 1988). The solution of eq. (14) has either one or three real roots. If the solution has three real roots, the lowest positive root corresponds to the Z of the liquid and the highest root corresponds to the Z of the vapor.

3.2. Gibbs minimization method (GM)

In GM method the Gibbs energy of mixing is minimized with respect to the vapor and the liquid compositions simultaneously at a given temperature and pressure. This requires information about the Gibbs energy of mixing and its first composition derivative. The reduced Gibbs energy of mixing ($\phi = \Delta G_m/RT$) for the SRK EOS is given by

$$\phi = X_1\ln X_1 + X_2\ln X_2 + PV_m/RT - \ln(V_m - b_m)$$

$$- (a_m/RTb_m)\ln[(V_m + b_m)/V_m]$$

$$- X_1\{PV_1/RT - \ln(V_1 - b_1)$$

$$- (a_1/RTb_1)\ln[(V_1 + b_1)/V_1]\}$$

$$- X_2\{PV_2/RT - \ln(V_2 - b_2)$$

$$- (a_2/RTb_2)\ln[(V_2 + b_2)/V_2]\}. \quad (16)$$

The derivative of ϕ with respect to compositions are evaluated from eq. (16). The derivative of volume needed in these calculations are determined from the EOS [eq. (3)]. Volumes of the liquid and vapor phases are obtained as described above in the FM using a Newton–Raphson numerical scheme. Equilibrium compositions of liquid and vapor phases are calculated using the Newton–Raphson derivative technique (Press et al., 1992). Similar to the fugacity method, this method requires suitable starting values of the compositions to solve for the equilibrium compositions of the vapor and the liquid phases numerically. If the starting values of the compositions are far away from the final values, there may be a convergence problem in the numerical scheme in getting the equilibrium values of the compositions.

3.3. Area method (AM)

In this method, the area, A, confined between the tie line and the nonuniformly continuous curve ϕ must be positive in its absolute value (see Fig. 1). This area corresponds to the equilibrium compositions X_I and X_{II} and has been defined as that area which lies
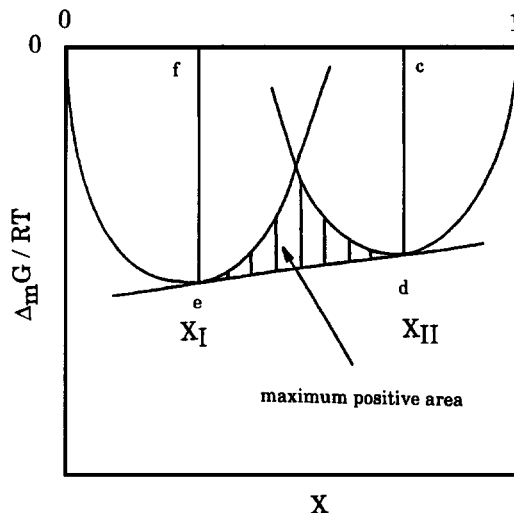

Fig. 1. Molar Gibbs energy of mixing for a binary fluid mixture at a given temperature and pressure. X_I and X_{II} represent equilibrium compositions.

between the trapezoid $cdef$ and the integrated Gibbs free energy curve from X_I to X_{II}. More explicitly,

$$A(X_a, X_b) = |[\phi(X_b) + \phi(X_a)]$$

$$\times [(X_b - X_a)/2]| - \left|\int_{X_a}^{X_b}\phi(X)\,dX\right| \quad (17)$$

then $A(X_I, X_{II}) = \max A(X_a, X_b)$,

subject to $A > 0$. $\quad (18)$

Note that (X_I, X_{II}) represent phase equilibrium compositions of liquid and vapor phases of the mixture only if the area is positive and maximum. In this method two points (X_a and X_b) in the composition range are sought such that the difference between the absolute area of the trapezoid evaluated at these two points and the absolute area of the curve ϕ integrated between these same points should be at maximum and positive (Eubank et al., 1992). The calculation of phase equilibria using the area method requires only the knowledge of ϕ given by eq. (16). Since the integral of eq. (17) cannot be integrated analytically using an equation of state, we resort to numerical integration technique. In eq. (17), integration over the Gibbs free energy ϕ is performed using the trapezoidal rule, which can be made as accurate as possible by reducing the mesh size in the numerical integration. This integration scheme of AM guarantees global minimum of the Gibbs free energy because it retains the sufficient condition.

4. RESULTS AND DISCUSSION

In this section we consider examples of two binary mixtures, namely, CO_2–butane and CO_2–propane for which extensive and accurate experimental data are available. Comparisons of the three methods for calculating vapor–liquid-phase equilibria are presented for each system over a range of conditions. Table 1

Table 1. Parameters of the pure fluids used in the SRK EOS

System	T_c (K)	P_c (MPa)	ω
CO_2	304.2	7.398	0.225
Butane	425.2	3.796	0.193
Propane	369.8	4.25	0.152

lists the parameters (critical temperature, critical pressure and acentric factor) of CO_2, butane and propane (Reid *et al.*, 1988). The parameter k_{12} was obtained from fitting isothermal VLE experimental data of binary mixtures at each temperature to the following objective function using FM:

$$\Delta X_1 = \frac{1}{n} \sum_{i=1}^{n} [ABS(X_{1,exp} - X_{1,calc}) \times 100/X_{1,exp}]_i$$

(19)

where $X_{1,exp}$ and $X_{1,calc}$ represent, respectively, the experimental and calculated values of the liquid-phase compositions at equilibrium, and n the number of data points. More explicitly, the error in mole fraction of the liquid phase, ΔX_1, is minimized by setting temperature and evaluating mole fraction of the vapor phase for the given saturation vapor pressure. Similar function was defined for the vapor-phase composition at equilibrium,

$$\Delta Y_1 = \frac{1}{n} \sum_{i=1}^{n} [ABS(Y_{1,exp} - Y_{1,calc}) \times 100/Y_{1,exp}]_i$$

(20)

where $Y_{1,exp}$ and $Y_{1,calc}$ are, respectively, the experimental and calculated values of the vapor-phase compositions at equilibrium. However, ΔY_1 was not considered in the fit of k_{12}. Each calculation begins with the initial values of the compositions taken from the experiment. The percentage average absolute deviation between calculated and experimental results for the liquid- and vapor-phase compositions (i.e., ΔX_1, and ΔY_1) at each temperature are given in Table 2. Note that the points close to the critical loci and for which FM is unable to predict phase equilibria are not taken into the fit. The determined values of k_{12} are also listed in Table 2. These values of k_{12} are then used

to generate the phase equilibrium results in GM and AM.

In order to check the efficiency of these numerical methods, we cite here the CPU time (central processing unit time at a HP700 series workstation) required in a typical run of the phase equilibrium calculation, say for CO_2-propane at $T = 344$ K and $P = 3$ MPa. In FM and GM calculations, the CPU time is ≈ 0.03 and 0.04 s, respectively, while in AM calculation, the CPU time is ≈ 0.08 s. In these calculations, the numerical accuracy in compositions in FM and GM is up to 8 significant figures, while that in AM is up to four significant figures. However, if one desires the accuracy of compositions up to three significant figures only, this CPU time in AM can be reduced significantly (≈ 0.04 s). It can be further reduced (≈ 0.02 s) if the accuracy required in compositions is up to two significant figures only.

Table 3 compares selected experimental VLE compositions of CO_2-butane system at $T = 278$ K and $T = 344$ K with those calculated from the three respective methods. The agreement between these methods at the subcritical temperature $T = 278$ K is very good. At pressures below the critical point of the isotherm $T = 344$ K (a supercritical temperature with respect to CO_2), $(P_c = 8.217$ MPa), the three methods gave similar results. However, in the vicinity of the critical point, FM produced a trivial solution at $P = 8.0668$ MPa, while both GM and AM predicted phase separation with similar results at this pressure. The failure of FM to predict VLE results close to the critical locus could be attributed to the formulation of its objective function given by eq. (19) which created convergence problems for the numerical subroutine.

We compare in Table 4 the compositions of the vapor and liquid phases of another mixture CO_2-propane at the supercritical temperatures of CO_2, $T = 311$ K and 344 K. Again, FM is unable to describe the vapor-liquid-phase equilibria in the vicinity of the critical point. Even GM is unable to predict phase separation in the vicinity of the critical locus which may be due to the iteration (or convergence) problem in minimizing the Gibbs energy of mixing. On the other hand, AM performs well even close to the critical point of the mixture.

To demonstrate the reliability of the SRK EOS/VDW MR model, Figs 2 and 3 compare vapor–

Table 2. Binary interaction parameter k_{12} for CO_2-butane and CO_2-propane systems

Mixture	T (K)	P-range (MPa)	No. of data points	k_{12}	ΔX_1 (liquid)	ΔY_1 (vapor)
CO_2-butane	278	0.3–3.7	10	0.128	2.7	0.6
	325	0.8–7.8	19	0.135	1.2	3.1
	344	1.1–8.2	15	0.143	1.8	1.6
	398	2.9–6.3	11	0.181	4.1	3.2
CO_2-propane	311	1.4–6.6	36	0.14	0.7	1.2
	328	2.1–6.4	20	0.147	1.3	2.2
	344	2.8–5.9	22	0.161	2.5	5.0
	361	3.8–4.9	8	0.189	1.0	9.6

Table 3. Vapor–liquid-phase equilibria of CO_2–butane at selected pressures (De Farnandez *et al.*, 1989)

	X_1 (liquid)				Y_1 (vapor)			
		Calculated				Calculated		
P (MPa)	Experimental	FM	GM	AM	Experimental	FM	GM	AM
$T = 278$ K								
0.3447	0.0390	0.0402	0.0402	0.0402	0.6062	0.6311	0.6310	0.6310
1.0480	0.1674	0.1748	0.1746	0.1748	0.8723	0.8751	0.8749	0.8749
1.3789	0.2303	0.2429	0.2426	0.2428	0.9015	0.9043	0.9041	0.9041
2.0684	0.4035	0.4014	0.4008	0.4013	0.9338	0.9362	0.9360	0.9361
3.1095	0.7538	0.7301	0.7284	0.7298	0.9636	0.9631	0.9630	0.9630
3.6611	0.9343	0.9216	0.9201	0.9213	0.9842	0.9818	0.9816	0.9817
$T = 344$ K								
1.1721	0.0295	0.0279	0.0279	0.0279	0.2643	0.2460	0.2457	0.2457
2.1787	0.1119	0.1144	0.1143	0.1144	0.5612	0.5544	0.5543	0.5543
3.1302	0.1967	0.1966	0.1966	0.1967	0.6621	0.6650	0.6649	0.6649
5.8192	0.4347	0.4395	0.4393	0.4396	0.7612	0.7707	0.7707	0.7706
6.5431	0.5047	0.5109	0.5106	0.5108	0.7716	0.7782	0.7782	0.7778
7.2257	0.5732	0.5840	0.5835	0.5841	0.7729	0.7780	0.7781	0.7783
7.8255	0.6343	0.6595	0.6588	0.6469	0.7700	0.7660	0.7662	0.7654
8.0668	0.6674	0.7135	0.7023	0.6941	0.7531	0.7135	0.7482	0.7471
8.2170	0.7200	0.7037	—	—	0.7200	0.7037	—	—

Table 4. Vapor–liquid-phase equilibria of CO_2–propane at selected pressures (Niesen and Rainwater, 1990)

	X_1 (liquid)				Y_1 (vapor)			
		Calculated				Calculated		
P (MPa)	Experimental	FM	GM	AM	Experimental	FM	GM	AM
$T = 311$ K								
1.4890	0.0199	0.0201	0.0199	0.0199	0.1100	0.1009	0.1000	0.1000
2.0298	0.0858	0.0864	0.0862	0.0862	0.3243	0.3199	0.3192	0.3192
3.1412	0.2285	0.2301	0.2298	0.2297	0.5454	0.5431	0.5426	0.5425
4.3223	0.3988	0.3973	0.3968	0.3966	0.6680	0.6607	0.6603	0.6602
5.4861	0.5794	0.5792	0.5782	0.5783	0.7384	0.7334	0.7330	0.7329
6.0907	0.6703	0.6783	0.6774	0.6772	0.7705	0.7636	0.7633	0.7631
6.5286	0.7405	0.7547	0.7535	0.7493	0.7894	0.7791	0.7790	0.7707
6.6396	0.7600	0.7757	0.7751	0.7698	0.7910	0.7757	0.7751	0.7765
6.6777	0.7695	0.7771	—	0.7733	0.7867	0.7771	—	0.7760
6.7018	0.7800	—	—	—	0.7800	—	—	—
$T = 344$ K								
2.8910	0.0214	0.0183	0.0181	0.0182	0.0650	0.0523	0.0519	0.0519
3.5301	0.0800	0.0774	0.0773	0.0773	0.1934	0.1815	0.1812	0.1812
4.7608	0.1981	0.1989	0.1988	0.1987	0.3417	0.3320	0.3318	0.3318
5.0538	0.2274	0.2304	0.2302	0.2302	0.3640	0.3550	0.3547	0.3547
5.5889	0.2862	0.2933	0.2930	0.2930	0.3885	0.3849	0.3847	0.3847
5.8936	0.3341	0.3372	0.3368	0.3373	0.3839	0.3909	0.3907	0.3905
5.9191	0.3410	0.3523	0.3405	0.3413	0.3755	0.3523	0.3405	0.3904
5.9315	0.3711	0.3724	0.3724	0.3535	0.3740	0.3724	0.3724	0.3901

liquid-phase equilibria for CO_2–butane and CO_2–propane, respectively. These calculations are based on AM using the optimized k_{12} parameter listed in Table 2. As can be seen from these figures, predictions are in good agreement with experimental results.

Finally, in Figs 4 and 5 we compare percentage deviation of our calculation from experiment for CO_2–propane system. Calculations of compositions for the vapor and liquid phases are performed using AM and FM. Results presented in Fig. 4 are at $T = 311$ K, and those in Fig. 5 are at $T = 344$ K (these temperatures correspond to the supercritical conditions for CO_2). It is seen that in the vicinity of the critical loci of the mixtures (at relatively high pressures), AM predictions are more accurate than those of FM, while they are similar at low pressures. More specifically, for the same number of data points, the FM and AM predictions for ΔX_1 at $T = 311$ K are 0.93 and 0.58, respectively, while their predictions for ΔY_1 at the same temperature are 1.63 and 1.45, respectively. Likewise, at $T = 344$ K their respective
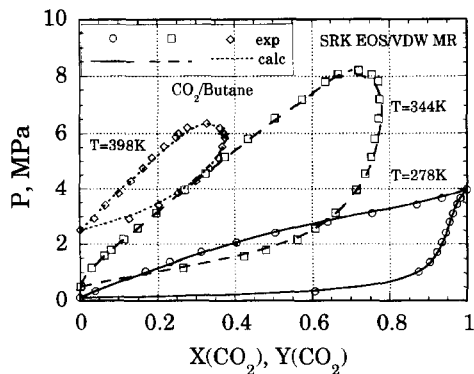
Fig. 2. Vapor–liquid-phase equilibria of CO_2–butane using SRK EOS/VDW MR from area method and experiment (De Farnandez et al., 1989).
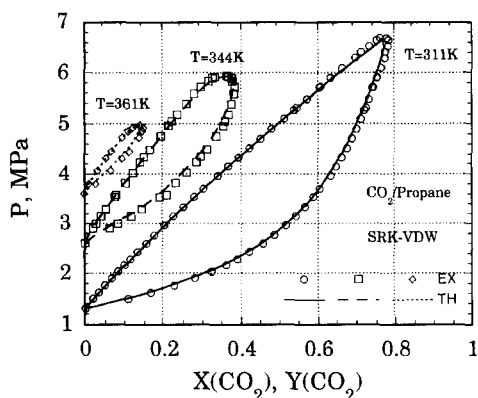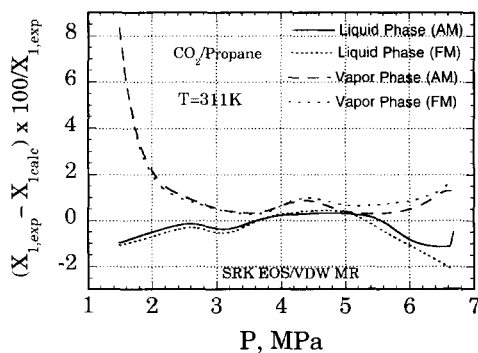

Fig. 5. Deviations in compositions of liquid and vapor phases of CO_2–propane at $T = 344$ K using SRK EOS/VDW MR and experiment (Niesen and Rainwater, 1990).

Fig. 3. Vapor–liquid-phase equilibria of CO_2–propane using SRK EOS/VDW MR from area method and experiment (Niesen and Rainwater, 1990).

Fig. 6. Deviations in compositions of liquid and vapor phases of CO_2–butane at $T = 344$ K using SRK EOS/VDW MR and experiment (De Farnandez et al., 1989).

comparisons. Another point to be mentioned here is the accuracy of the SRK EOS/VDW MR model based on AM calculations. Figures 4 and 5 show a discrepancy between experimental and calculated results for compositions at some pressures, suggesting that the pressure dependence of the compositions is not described accurately. This is also borne out from the above percentage deviations between calculated and experimental results based either on FM or AM. Since the AM method is accurate, these remaining discrepancies, which could not be distinguished in Fig. 3, might be attributed to the inadequate representation of thermodynamic properties of the mixtures by SRK EOS/VDW MR model. Similar behavior can be also seen in Fig. 6 for CO_2–butane system at $T = 344$ K. In this case, the FM and AM predictions for ΔX_1 are 2.8 and 2.2, respectively, while their values for ΔY_1 are 2.0 and 1.6, respectively.

Fig. 4. Deviations in compositions of liquid and vapor phases of CO_2–propane at $T = 311$ K using SRK EOS/VDW MR and experiment (Niesen and Rainwater, 1990).

5. CONCLUSIONS

In this paper we have presented three methods for calculating the vapor–liquid-phase equilibria in several binary fluid mixtures using the SRK EOS/VDW MR model. Comparisons of different sets of calculations on the binary mixtures CO_2–butane and

values for ΔX_1 are 3.48 and 3.11, while their values for ΔY_1 are 5.54 and 5.24. Note that these values of ΔX_1 and ΔY_1 are slightly different from those given in Table 2 because some data points, for which the values of the vapor- and liquid-phase compositions are found to be the same, are excluded from these
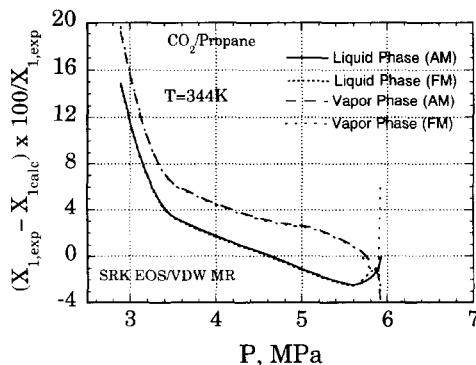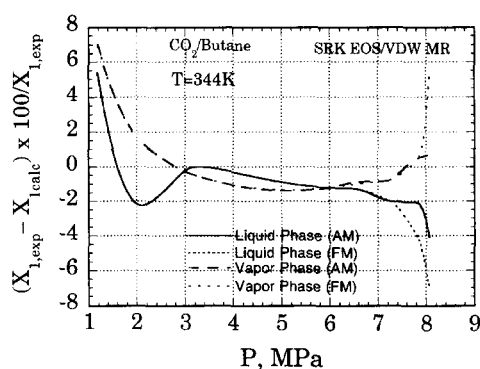
CO$_2$–propane in the previous section suggest that close to the critical locus of the mixtures AM performs better than either FM or GM, while GM performs better than FM. In all other situations including the subcritical conditions, all three methods predict similar results for the vapor- and liquid-phase compositions. A similar situation might hold for the more nonideal and asymmetric fluid mixtures. It can be concluded that (a) AM does not need any starting values, (b) it does not involve derivatives of the free energy, and (c) it is more accurate than the other two tested methods for calculating the vapor–liquid-phase behavior very close to the critical loci of the mixtures. This investigation provides a further quantitative support to the previous studies (Eubank et al., 1992) in examining the accuracy of AM for describing phase equilibria in binary mixtures.

It is straightforward to extend FM or GM to multicomponent mixtures, while AM becomes numerically more involved. For the proper initial values of the variables, both FM and GM are sufficiently accurate to be implemented in the wide range of calculations for phase equilibria in mixtures. Once values for the binary interaction parameter are determined, AM can be then used to provide a check on FM and GM calculations in the vicinity of the critical locus of the mixtures. In general, AM is an excellent and efficient technique to locate phase equilibria in fluid mixtures.

Since AM is very successful in predicting the vapor–liquid-phase equilibria in these mixtures, the remaining discrepancy between calculated results and experimental data, as illustrated in Figs 4–6, might be attributed to the inadequate representation of thermodynamic properties by the SRK EOS/VDW MR model.

In our future studies, we plan to examine the performances of these numerical approaches by developing more accurate equations of state and accurate mixing rules. We then apply them to correlate and predict thermodynamic properties in addition to the phase equilibria of highly asymmetric binary, ternary and multicomponent fluid mixtures, with particular emphasis on the supercritical conditions of the mixtures.

NOTATION

a_m	energy parameter
A	area
b_m	size parameter
G_m	molar Gibbs energy of the mixture, J/mol
k_{12}	binary interaction parameter
P	pressure
R	gas constant
T	absolute temperature
V	total molar volume
X_1	liquid-phase composition of the first component
Y_1	vapor-phase composition of the first component

Greek letters

α	constant in the equation of state
ϕ	reduced molar Gibbs energy of mixing
ω	acentric factor

Abbreviations

EOS	equation of state
IMSL	IMSL, Inc., supplied package of subroutines
MR	mixing rules
RK	Redlich–Kwong EOS
SRK	Soave–Redlich–Kwong EOS
VDW	van der Waals

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