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Equation of state taking into account dipolar interactions and association by hydrogen bonding: II—Modelling liquid–vapour equilibria in the H_2O–H_2S, H_2O–CH_4 AND H_2O–CO_2 systems

Erwan Perfetti [a,*,1], Régis Thiery [b], Jean Dubessy [a]

[a] G2R, Nancy-Université, CNRS, CREGU, BP 239, 54506, Vandoeuvre-les-Nancy, France
[b] Laboratoire Magma et Volcans, UMR 6524, Université Blaise Pascal, 5, rue Kessler, 63038-Clermont-Ferrand Cedex, France

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ABSTRACT

The CPAMSA equation of state proposed in Perfetti et al. [Perfetti, E., Thiery, R., Dubessy, J., 2008-this issue. Modelling liquid–vapour equilibria with an equation of state taking into account dipolar interactions and association by hydrogen bonding. I—Application to water and hydrogen sulphide. Chem. Geol.](2008-this issue) results in a better reproduction of the thermodynamic properties of pure water and pure hydrogen sulphide than obtained using the classical CPA or SRK equations of state along the vapour–liquid equilibrium. It considers three contributions. The first contribution represents the reference Van der Waals fluid which is modelled by the SRK cubic EOS. The second contribution accounts for association through hydrogen bonding and is modelled by a term derived from Cubic Plus Association (CPA) theory. The third contribution corresponds to the dipolar interactions and is modelled by the Mean Spherical Approximation (MSA) theory. This present paper extends the CPAMSA equation of state for multi components systems, thus simple mixing rules between dipolar molecules are proposed to model the H_2O–H_2S binary system using a symmetrical approach. Binary interaction parameters which steps in the cubic terms (i.e. the Van der Waals mixing rule) are optimized on experimental solubility data of gas in aqueous solutions. Calculated phase equilibria in the H_2O–H_2S, H_2O–CO_2, H_2O–CH_4 systems reproduced the experimental data within 7% of average accuracy. Except for the H_2O–CH_4 system, binary interactions parameters estimated by fitting experimental data are closed to zero.

1. Introduction

Modelling fluid rock interactions as well as mixing and unmixing phenomena in geological processes (acid gases storage, metamorphic fluids studies) requires robust equation of state (EOS) which must be applicable to systems containing water, gases and salts in a large scale of temperature and pressure. Cubic EOS are not accurate enough to model the PVTX properties of fluid rich in water, due to hydrogen bonding which occur between two molecules of H_2O. These EOS, which are based on the Van der Waals theory, do not take account the association energy induced by hydrogen bonding.

In the first companion paper (Perfetti et al., 2008-this issue) an equation of state, formulated at the level of Helmholtz energy, has been proposed for dipolar fluids and/or associated pure fluids. Dipolar interactions contribution is based on equations derived from MSA theory and the association from CPA-SAFT theory. This model demonstrated to be accurate in the modelling of liquid–vapour phase equilibrium of pure water and pure hydrogen sulphide system. In addition, it was demonstrated that this equation of state was accurate also in the single phase field of water, in the 25–400 °C and 1–10 kbar temperature–pressure range. Therefore, the aim of this paper is to demonstrate the capacity of this equation of state to model liquid–vapour equilibrium in binary systems such as H_2O–H_2S, H_2O–CO_2 and H_2O–CH_4.

2. Theory

2.1. Equation of state

The CPAMSA model is written in terms of Helmholtz energy that is more detailed in Perfetti et al. (2008-this issue):

$$A(T,V,N) = A(T,V,N)^{\mathrm{VdW}} + A(T,V,N)^{\mathrm{dd}} + A(T,V,N)^{\mathrm{association}} \quad (1)$$

The Van der Waals interactions (Eq. (2)) which correspond to the reference fluid are described by a cubic equation of state, here the Soave–Redlich–Kwong equation of sate (Soave, 1972):

$$A(T,V,N)^{\mathrm{SRK}} = -\ln(v-b) - \frac{a(T)}{bRT}\ln\left(\frac{v+b}{v}\right) \quad (2)$$

* Corresponding author.
E-mail address: erwan.perfetti@gmail.com (E. Perfetti).
[1] Present address: Institut Français du Pétrole, Reservoir Engineering Division R031 Petrophysics Department 1-4 Av de bois Préau 92500 Rueil Malmaison, France.

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The variation of the attractive parameter a with temperature is a function of reduced temperature and the acentric factor of the component according to Eq. (3) issued from Soave (1972):

$$a(T) = a_0[1 + c(1 - \sqrt{T/T_c})]^2$$
$$c = 0.48508 + 1.55171\omega - 0.15613\omega^2 \quad (3)$$

Parameters a_0 and b are given for SRK by Soave (1972) and are related to pseudo-critical parameters (Eq. (4)). The pseudo-critical point is the critical point which would have a molecule without dipolar interaction and associative attraction (Perfetti et al., 2008-this issue).

$$a_0 = 0.42747\frac{(RT_c^*)^2}{P_c^*}$$
$$b = 0.08664\frac{RT_c^*}{P_c^*} \quad (4)$$

Only Van der Waals interactions occur between molecules of the reference fluid, reference fluid is assumed to be typical of rare gases, thus, acentric factor of reference fluid is taken equal to zero in the CPAMSA model.

Dipolar interactions are modeled using equations established by Liu et al. (1999) and Gao et al. (1999) of the non-primitive MSA theory and perturbation theory. It is recalled in Eq. (5).

$$A^{dd} = \frac{A_2^{dd}}{1 - \frac{A_3^{dd}}{A_2^{dd}}} \text{ where}$$
$$\frac{A_2^{dd}}{RT} = -\frac{2\pi}{3d^3}\rho\left(\frac{x_{dip}\mu^2}{kT(4\pi\varepsilon_0)}\right)^2 I_{dd} \quad (5)$$
$$\frac{A_3^{ddd}}{RT} = \frac{4\pi^2}{27d^3}\rho^2\left(\frac{x_{dip}\mu^2}{kT(4\pi\varepsilon_0)}\right)^3 I_{ddd}$$

where x_{dip} is the mole fraction of dipolar moment μ, d is the molecular diameter, ρ is the number density, I_{dd} and I_{ddd} are integrals of correlation functions for two and three dipoles calculated by Twu and Gubbins (1978).

$$I_{dd} = \left(\frac{1}{3}\right)\frac{1 + 0.18158\rho^* - 0.11467\rho^{*2}}{1 - 0.49303\rho^* + 0.06293\rho^{*2}} \quad (6)$$
$$I_{ddd} = \left(\frac{5}{24}\right)\frac{1 + 1.12754\rho^* + 0.56192\rho^{*2}}{1 - 0.05495\rho^* + 0.13332\rho^{*2}}$$

with $\rho^* = \rho \cdot x_d \cdot d^3$, $\rho = N_A/v$.

The Helmholtz energy for a molecule with M association site corresponding to the association between molecules is taken from Kontogeorgis et al. (1996) and is detailed in Eqs. (7)–(10):

$$\frac{A^{assoc}}{RT} = \sum_A\left[\ln(X_{nb}^A) - \frac{X_{nb}^A}{2}\right] + \frac{1}{2}(M) \quad (7)$$

$$X_{nb}^A = \left(1 + \rho N_{Av}\sum_B X_{nb}^B \Delta_{hb}^{AB}\right)^{-1} \quad (8)$$

$$\Delta_{hb}^{AB} = g[\exp(\varepsilon/kT) - 1](\beta b) \quad (9)$$

$$\text{with } g = \frac{2 - \frac{b}{4v}}{2\left(1 - \frac{b}{4v}\right)^3} \quad (10)$$

X_{nb}^A is the mole fraction of non hydrogen bonded molecule to any site A, and M the number of sites, summation being done over all association sites. Δ_{hb}^{AB} is the association strength where g is the correlation function, ε is the energy of hydrogen bonds between site A and site B of two molecules, b the covolume (exclusion volume) of the cubic EOS and β is an empirical parameter.

These equations are established with pure components for which the value of parameters depends on the component. Parameters of pure components used in this studies have been optimized in Perfetti et al. (2008-this issue) for H_2O and H_2S. Parameters for CO_2 and CH_4 are taken from Prausnitz et al. (1999). All parameters are given in Table 1.

2.2. Mixing rules

In the different systems studied in this work (H_2O–H_2S, H_2O–CO_2, H_2O–CH_4), only water molecules are involved in hydrogen bonding since H_2S, CH_4 and CO_2 do not develop association sites. Therefore, it is not necessary to define mixing rules relative to the association part of the model for these systems. On the contrary, the cubic part of each reference fluid is common to all components, which justifies the definition of mixing rules. In the same way, H_2O and H_2S are two dipolar molecules with different dipolar moments, thus, the H_2O–H_2S system needs mixing rule for the formulation of dipolar contribution.

2.2.1. SRK reference fluid and mixing rules

Mixing rules chosen in this work are the usual mixing rules of cubic EOS:

$$a = \sum_i\sum_j a_{ij}x_ix_j \quad \text{with } a_{ij} = \sqrt{a_ia_j}(1 - k_{ij}) \quad \text{where } \begin{matrix} k_{i=j} = 0 \\ k_{i\neq j} \neq 0 \end{matrix} \quad (11)$$
$$b = \sum_i b_ix_i$$

If the interactions other than Van der Waals are modelled correctly, a small value for the binary interaction parameter is expected.

The methane molecule has an acentric factor close to zero (ω=0.013, Pitzer, 1955) and its permanent electric moment is an octopole which is expected to interact weakly with water molecules. Therefore, it is reasonable to assume that methane could be modelled only by the SRK EOS since other energetic contributions are neglected and its parameters corresponding to pure CH_4.

The system H_2O–CO_2 is *a priori* more complicated since this molecule has a quadrupole moment. Contribution of quadrupolar interactions and quadrupole–dipole interactions to the Helmholtz energy can be modelled using equations from Gubbins and Twu (1978) and Twu and Gubbins (1978) which are recalled by Duan et al. (2006). In order to not add another degree of complexity to the model and because quadrupolar interactions and quadrupole–dipole interactions are weaker than dipolar interactions, it was assumed these contributions could be neglected. In addition, if the Helmholtz energy of the reference fluid relative to CO_2 is taken as CO_2 itself, this implies that quadrupolar interactions are taken into account by the SRK EOS of pure CO_2. Only the quadrupole–dipole interactions are not specifically taken into account. However, the binary interaction parameter between CO_2 and the Van der Waals reference fluid of water is expected to take part in this energetic contribution.

2.2.2. Dipolar interactions and their mixing rules

For the H_2O–H_2S system, which is a fluid mixture of two molecules characterized by their dipole moment μ_1 and μ_2, a straightforward

Table 1
Values of parameters for pure components used for calculations in binary mixture

		Cubic		Dipolar		Association	
Compound	a (J m^3)	b (cm^3/mol)	ω	ε/k (K)	κ	d (Å)	μ (D)
H_2O	0.0871	13.851	0	2496	0.026	3.2	2.2
H_2S	0.3929	29.01	0	–	–	2.50	1.11
CO_2	0.3703*	29.86*	0.239	–	–	–	–
CH_4	0.2334*	29.68*	0.011	–	–	–	–

Superscript (*) indicates that values have been calculated from critical parameters in Prausnitz et al. (1999).

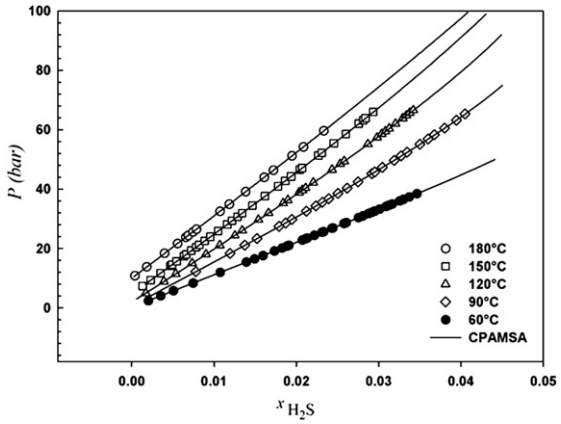

Fig. 1. Experimental and calculated solubility of hydrogen sulphide in water for different isotherms with CPAMSA as a function of pressure.

mixing rule is defined for μ_i^2. Considering an average value of this term weighted by composition of each component, the mixing rule is:

$$\mu_m^2 = x_1\mu_1^2 + x_2\mu_2^2 \tag{12}$$

If the first component is related to water, the mole fraction of dipoles depends on the bulk concentration of water $x(H_2O)$ and the mole fraction of non-bonded molecules X_{nb}. Consequently, the mixing rule relative to dipole moments in the system H_2O–H_2S is given by Eq. (13):

$$\mu_m^2 = x(H_2O)X_{nb}\mu_{H_2O}^2 + x_{H_2S}\mu_{H_2S}^2 \tag{13}$$

The other parameter is relative to the size of the molecule d. The mixing rule related to parameter b is an arithmetic mixing rule. As parameter b has the dimension of a volume, these mixing rules can be written as a function of two parameters:

$$b_i = \delta_i^3 \quad \text{and} \quad b_m = x_1(\delta_1)^3 + x_2(\delta_2)^3 \tag{14}$$

By analogy with this mixing rule, the mixing rule over the dimension d_m of the dipole moment is the following:

$$d_m^3 = x_1(d_1)^3 + x_2(d_2)^3 \tag{15}$$

If we refer to the number of dipolar structures which are not involved in hydrogen bonds and so have only dipolar interaction in addition to Van der Waals interactions, the mixing rules relative to the dimension of the dipole moment will be the following:

$$d_m^3 = x(H_2O)X_{nb}\cdot(d_1)^3 + x_{H_2S}(d_{H_2S})^3 \tag{16}$$

Therefore, the model contains only one parameter, the binary interaction parameter of the cubic part.

Table 2
Values of binary interaction parameters optimized for different isotherms on solubility data in the H_2O–H_2S system, and related standard deviations in percent

T (°C)	kij	σ xH_2S (%)
60	0.018	1.7
90	0.023	1.3
120	0.023	1.4
150	0.021	1.2
180	0.013	1.4

3. Experimental data

The fitting procedure of binary interaction parameters kij requires experimental data of solubilities or experimental binary phase equilibria in a wide range of temperatures, pressures and compositions. Consistent experimental data for the binary systems H_2O–H_2S and H_2O–CO_2 have been reviewed by Duan et al. (1996) and Dubessy et al. (2005) from which data are selected for fitting. Since kij

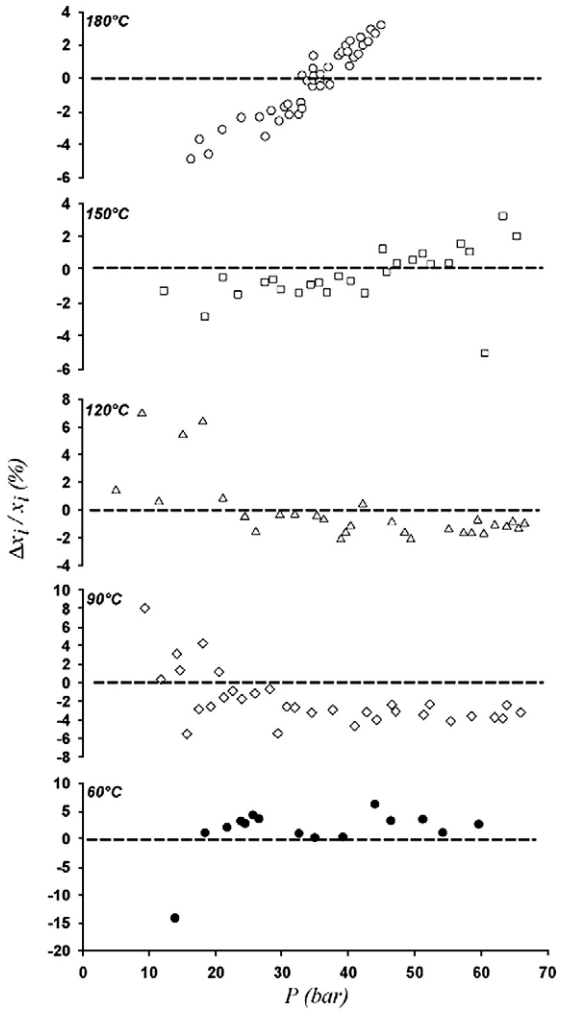

Fig. 2. Deviations between calculated and experimental solubility of hydrogen sulphide for each isotherm obtained with CPAMSA as a function of pressure after optimization of binary interaction parameters.

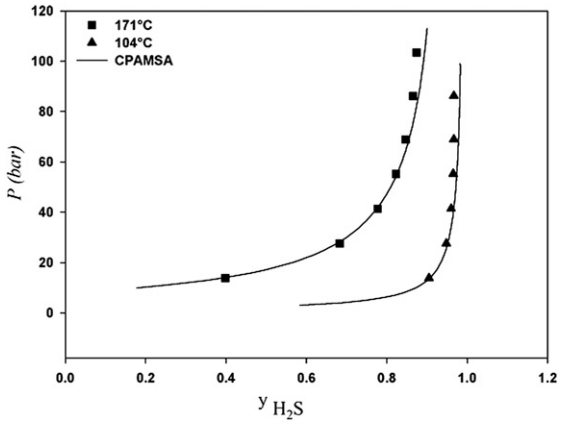

Fig. 3. Experimental and calculated composition of the vapour phase (H_2S concentration) in equilibrium with liquid phase in the system H_2O–H_2S for different isotherms with CPAMSA as a function of pressure.

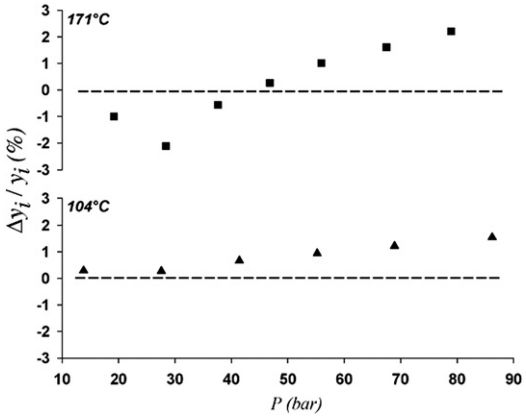

Fig. 4. Deviations between calculated and experimental composition of hydrogen sulphide in vapour phase in equilibrium with liquid phase in the system H_2O–H_2S as a function of pressure.

optimization are performed along isotherm (*P*, *x* diagrams) in view to obtain a classical function with temperature (Daridon 1992), much data are needed for each isotherm.

Thus, for the binary system H_2O–H_2S, data selected from Dubessy et al. (2005) are taken from Lee and Mather (1977), Selleck et al. (1952), Chapoy et al. (2005).

For the binary system H_2O–CO_2, data are more numerous since it is a more studied classical system. Relevant data selected from Dubessy et al. (2005) are those of Zel'vinskii (1937), Wiebe and Gaddy (1939, 1941), Prutton and Savage (1945), Tödheide and Franck (1963), Takenouchi and Kennedy (1964), Matous et al. (1969), Malinin and Savelyeva (1972), Malinin and Kurovskova (1975), Drummond (1981), Zawisza and Malensinska (1981), Gillepsie and Wilson (1982), Briones et al. (1987), Muller et al. (1988), Nighswander et al. (1989), Sako et al. (1991),Dohrn et al. (1993),D'Souza et al. (1988), Bamberger et al. (2000), and Vorholz et al. (2000).

Consistent experimental data of composition at phase equilibrium in the system H_2O–CH_4 have been reviewed by Austergard et al.

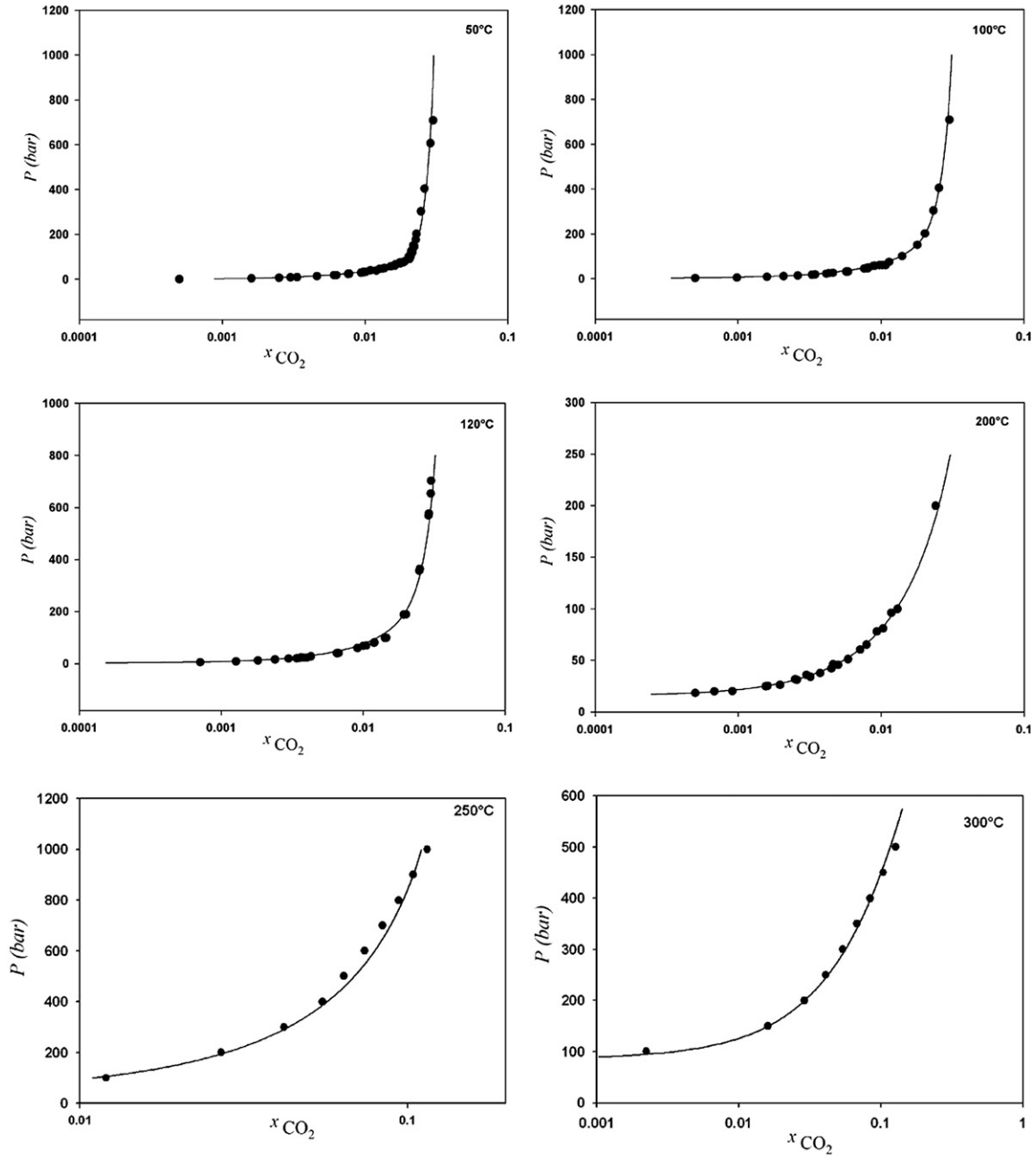

Fig. 5. Experimental and calculated solubility of carbon dioxide in water for different isotherms with CPAMSA as a function of pressure.

Table 3
Values of binary interaction parameters optimized for different isotherms on solubility data in the H_2O–CO_2 system, and related standard deviations in percent

T (°C)	kij	σ xCO_2 (%)
50	0.047	5.0
100	0.063	4.9
120	0.069	7.0
200	0.044	5.0
250	−0.09	4.7
300	−0.17	10.3

(2006). Retained data for *kij* fitting are from Culberson and McKetta (1951), O'Sullivan and Smith (1970), Sultanov et al. (1972) and Olds et al. (1942). Since a large number of consistent experimental data are required for each isotherm, our optimizations are limited up to 180°C in the two phases and single phase domains.

4. Results and discussion

All calculations are performed with LOTHER software (Thiery, 1996) which allows flash calculations. Standard deviations obtained are given by Eq. (17).

$$\sigma = \frac{1}{n}\sum_{i=1}^{n} \left| \frac{\xi_i^{exp} - \xi_i^{cal}}{\xi_i^{exp}} \right| \quad (17)$$

4.1. System H_2O–H_2S

The binary interaction parameter is determined at each temperature from 60 to 180 °C only on experimental solubilites of H_2S in water (liquid phase of the equilibrium) as few data exist in vapour phase. Its value varies slightly with temperature but remains small. This indicates that the dipolar interactions are correctly modelled. The positive value of the binary interaction parameter decreases slightly the attraction parameter of the end-members of the reference fluid.

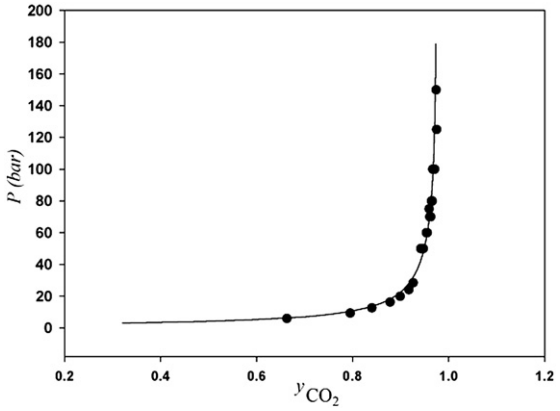

Fig. 7. Experimental and calculated composition of carbon dioxide in vapour phase in equilibrium with liquid phase in the system H_2O–CO_2 for different isotherms with CPAMSA at 120 °C as a function of pressure.

The quality of the fit is demonstrated by the projection of isotherms in a pressure-composition plot of the aqueous liquid phase (Fig. 1). More precisely, the errors in percent are plotted for each isotherm (Fig. 2). Except for isotherm at 180 °C, there is no trend of error with pressure. Values of *kij* and average error on solubility of H_2S in water are given in Table 2.

Binary interaction parameters obtained with CPAMSA on this system must be compared to these calculated by Evelein et al. (1976) on the same binary system with the SRK model since their *kij* values are about ten times higher.

Although binary interaction parameters were not optimized on vapour phase, it is worth noting that the values predict correctly the composition of the vapour phase as shown are shown on Fig. 3 for isotherms 104 °C and 171 °C (Fig. 3). Errors on H_2S composition are plotted on Fig. 4 for these isotherms and average error remains smaller than 2.5%.

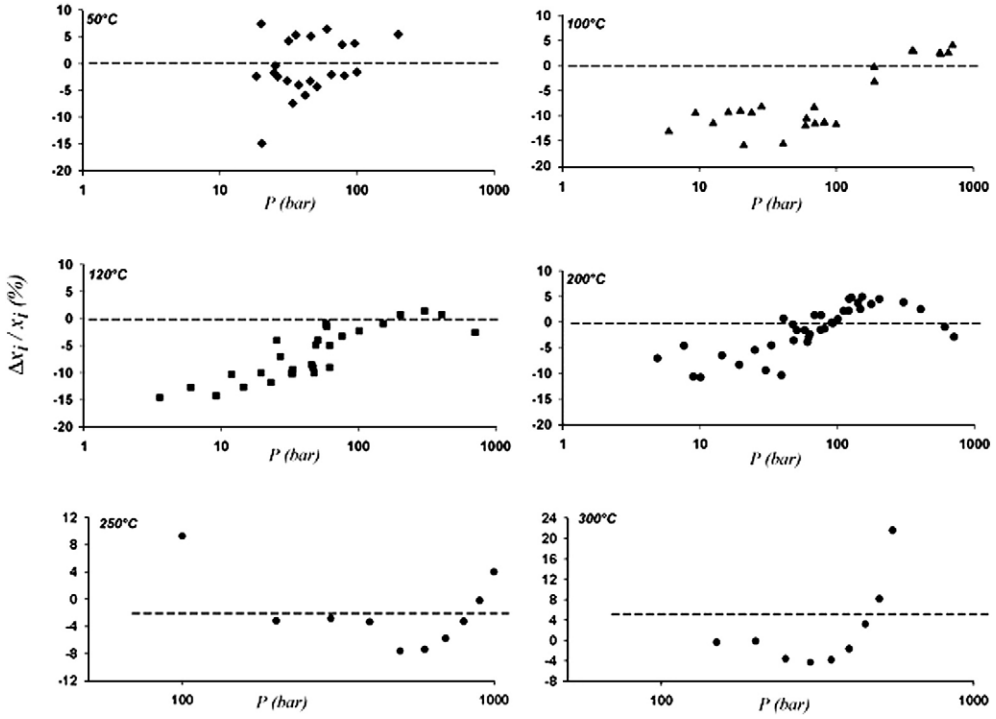

Fig. 6. Deviations between calculated and experimental solubility of carbon dioxide for each isotherm obtained with CPAMSA after optimization of binary interaction parameters.

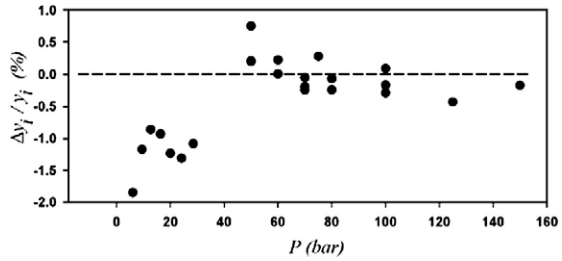

Fig. 8. Deviations between calculated and experimental composition of carbon dioxide in vapour phase in equilibrium with liquid phase in the system H_2O–CO_2 at 120 °C as a function of pressure.

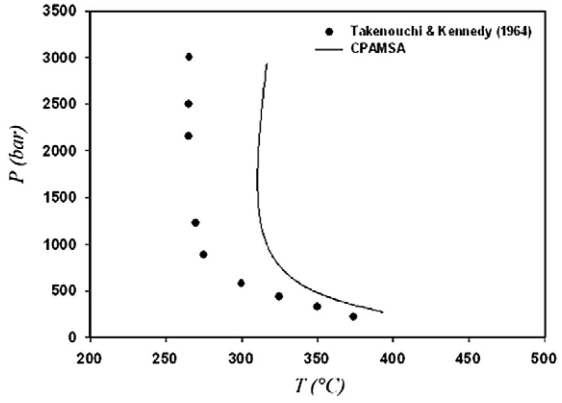

Fig. 9. Critical binary curve of H_2O–CO_2 system calculated and compared to experimental data.

4.2. System H_2O–CO_2

Binary interaction parameters are fitted on experimental solubilities along isotherm from 50 to 300 °C. This system requires mixing rules only in the cubic term since CO_2 develops neither association by hydrogen bonding nor dipolar interaction. Binary interaction parameters calculated are closed to zero and vary slightly with temperature. *kij* values calculated here are about ten times lower than these calculated by Evelein et al. (1976), on the same binary system with the SRK model. It is noteworthy that calculated solubilities of CO_2 in water with CPAMSA well fit experimental (Fig. 5) data with average statistical deviations are about 5% (Table 3). More precisely, the errors in percent are plotted for each isotherm (Fig. 6). Highest absolute values of binary interaction parameter are obtained for 250 °C and 300 °C. Compositions in the vapour phase have been calculated with *kij* given in Table 3 and experimental data are accurately fitted as shown by as example on the isotherm 120 °C (Figs. 7 and 8).

The critical binary curve of the H_2O–CO_2 system has been calculated and compared to experimental data of Takenouchi and Kennedy (1964) on Fig. 9. Even if calculation with CPAMSA overestimates temperature, the minimum of temperature is well predicted. This shifting could be explained by the overestimation of the critical temperature of pure water.

Table 4
Values of binary interaction parameters optimized for different isotherms on solubility data in the H_2O–CH_4 system, and related standard deviations in percent

T (°C)	*kij*	σ xCH_4 (%)
71	0.323	3.5
105	0.394	3.4
137	0.444	2.9
171	0.460	2.9
250	0.505	6.9

Table 5
Values of binary interaction parameters optimized for different isotherms on composition of data at equilibrium in vapour phase in the H_2O–CH_4 system, and related standard deviations in percent

T (°C)	*kij*	σ yH_2O (%)
71	1.18	6.1
104	1.15	4.9
137	1.13	2.7
171	1.10	3.1
204	1.01	2.5
238	0.96	2.2

4.3. System H_2O–CH_4

Contrary to previous binary systems where binary interaction parameters have been only fitted on composition in the liquid phase

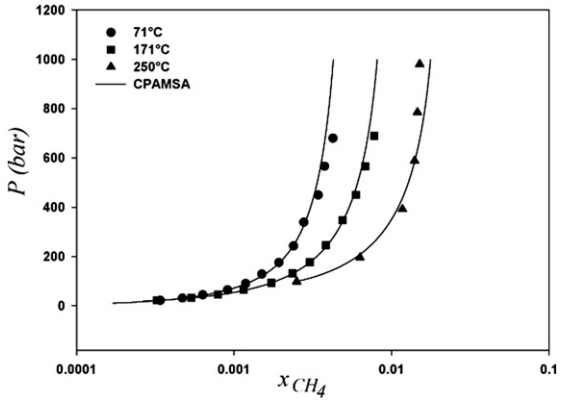

Fig. 10. Experimental and calculated solubility of methane in water for different isotherms with CPAMSA as a function of pressure.

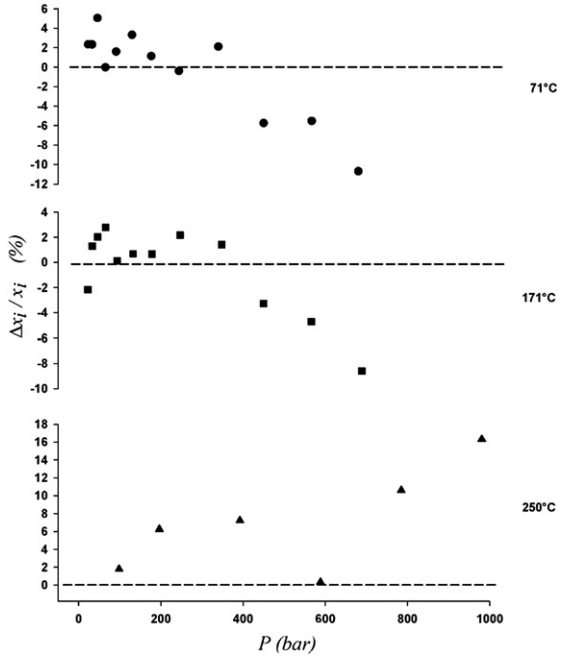

Fig. 11. Deviations between calculated and experimental solubility of methane in the aqueous liquid phase for each isotherm obtained with CPAMSA after optimization of binary interaction parameters as a function of pressure.

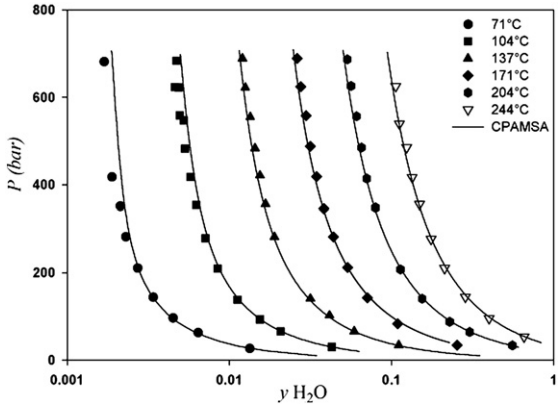

Fig. 12. Experimental and calculated concentration of water in the methane rich phase in equilibrium with the aqueous liquid phase for different isotherms with CPAMSA as a function of pressure.

at equilibrium, *kij* of the system H_2O–CH_4 have been optimized both on liquid phase and vapour phase along equilibrium. This is due to that binary interaction parameters calculated in liquid phase are strongly different from these calculated in vapour phase since a symmetric *kij* gives poor accuracies on solubilities. Nevertheless with these dissymmetric *kij*, average statistical deviations are between 2.2% and 6.9% (Tables 4 and 5), also, values are strongly dependant with temperature (Eqs. (18)) and (19)).

$$k_{ij}^{liq} = -5.791.10^{-6}T^2 + 6.001.10^{-3}T - 1.052 \quad (18)$$

$$k_{ij}^{gas} = -5.970.10^{-6}T^2 + 5.177.10^{-4}T + 1.170 \quad (19)$$

High values of binary interaction parameters is a particularity of H_2O–CH_4 system modelled with CPAMSA since previous systems have their values closed to zero and are symmetric (i.e. same value whatever the phase). Dissymmetry of *kij* in H_2O–CH_4 had been highlighted by Daridon (1992) with the Peng–Robinson EOS. Furthermore, Voutsas et al. (2000), using CPA EOS on the same system at equilibrium, have shown that binary interaction parameter optimized on vapour compositions are unable to correctly model liquid compositions: average statistical deviation on yCH_4 is 7% while it grow up to 23.7% in liquid phase. These values must be compared to those obtained here with the CPAMSA model which better fit experimental data: standard deviations with CPAMSA are between 6.1% and 2.2% depending on temperature.

Calculated isotherms in the (*P*, *x*) projection and deviation with experimental data are respectively shown on Figs. 10 and 11 whereas Figs. 12 and 13 are about vapour phase in the (*P*, *y*) projection. These figures show that maximal deviations are obtained for the highest pressures.

5. Conclusion

The CPAMSA equation of state was proposed to model phase equilibrium of pure water and pure hydrogen sulphide in Perfetti et al. (2008-this issue) by taking into account dipolar interactions and hydrogen bonding. Accurate reproductions of phase equilibria done with this new model have opened the way of mixture modelling with CPAMSA.

This present study focuses on binary systems (H_2O–H_2S, H_2O–CO_2 and H_2O–CH_4) which are the most common in geological fluids. For each binary system, the Van der Waals mixing rules are the well-known mixing rules for SRK equation of state. New mixing rules have been proposed for the dipolar interactions for the H_2O–H_2S system. Unique binary interaction parameter for the liquid and vapour phase have been found for the H_2O–CO_2 and H_2O–H_2S systems. Accuracy of results obtained on liquid and gaseous compositions at equilibrium in a wide range of temperatures and pressures with symmetric values of binary interaction parameter closed to zero. For the H_2O–CH_4 system, *kij* are dissymmetric however, composition of liquid and vapour phases are reproduced with good accuracy.

Results obtained in this present study open the way of modeling more realistic geological fluids (i.e. multicomponents fluids) with salts: since CPAMSA is built by summation of different energetic Helmholtz contributions of MSA and CPA, it is conceivable to add salts contributions from MSA, i.e. charge–charge and charge–dipole interaction contributions. Thus CPAMSA model should be used as well for fluid inclusions studies which involved many gases, water and salts, as calculations within fluid–rocks interaction software.

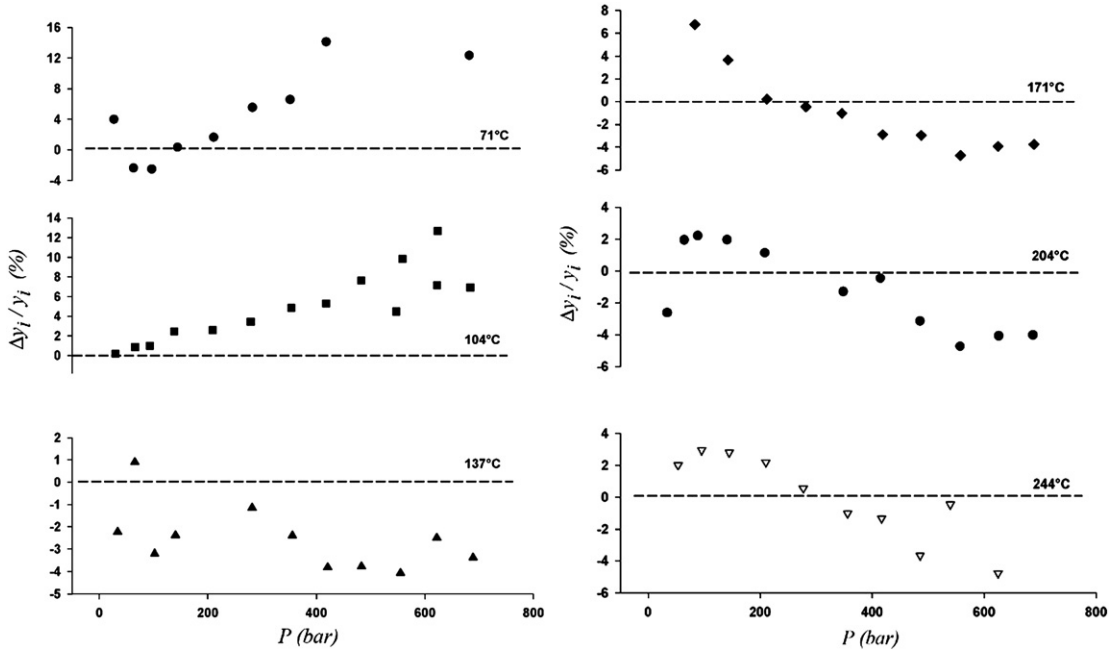

Fig. 13. Deviations between calculated and experimental concentration of water in the methane rich phase in equilibrium with the aqueous liquid as a function of pressure.

6. Constants and symbols

Indicated units (S.I. units) are given in ( ) and are used in the calculations. More common units are given in the text and mentioned here in [ ]

N_{Av}	Avogadro number = 6.02205 10^{23} (mol^{-1})
R	gas constant = 8.3144 ($J\ K^{-1}\ mol^{-1}$)
K	Boltzmann constant: 1.38066 10^{-23}($J\ K^{-1}$)
ε_0	vacuum permittivity: 8.854188 10^{-12} ($J\ C^{-2}\ m^{-1}$)
$4\pi\varepsilon_0$	1.112650 10^{-10} ($J^{-1}\ C^2\ m^{-1}$)
T	absolute temperature (K)
T_c	critical temperature (K); T_c^*: pseudo-critical temperature of the reference fluid (K)
P	pressure (Pa); [bar]
P_c	critical pressure; P_c^*: pseudo-critical pressure of the reference fluid (Pa); [bar]
$T_r = T/T_c$	reduced temperature of one component system;
V	volume occupied by N molecules (m^3)
V	molar volume ($m^3\ mol^{-1}$); [$cm^3.mol^{-1}$]
a	attractive parameter in the SRK EOS ($J\ m^3$)
b	covolume of the SRK EOS ($m^3\ mol^{-1}$); [$cm^3\ mol^{-1}$]
c	parameter of the SRK EOS function of ω
β	empirical parameter of the association strength
ω	acentric factor
$\rho = N_A/v$	number density (m^{-3})
ρ^*	density function
d	diameter of a molecule (m); [Å]
μ	dipole moment (subscript m for mixing) ($C\ m^{-1}$); [D]
ε	energy of hydrogen bond between A and B sites ($J\ mol^{-1}$);
I^{dd}–I^{ddd}	integrals of correlation functions for two (dd) and three (ddd) dipoles.
x_{dip}	molar fraction of dipole in the fluid.
X^A_{nb}	molar fraction of non-bonded (nb) molecule to site A
M	number of associating site per molecule
g	distribution function in association strength
x_i	molar fraction of component i in the liquid phase
y_i	molar fraction of component i in the vapour phase
kij	binary interaction parameter

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