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Equation of state taking into account dipolar interactions and association by hydrogen bonding. I: Application to pure water and hydrogen sulfide

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ABSTRACT

A new equation of state (EOS) is proposed to model liquid–vapor-equilibrium of pure components and water–gases systems in geological conditions relevant to diagenesis, hydothermal systems, anchimetamorphism and acid gases storage. This new equation of state is based on Statistical Association Fluid Theory and Mean Spherical Approximation Theory and proposes to take into account the respective association by hydrogen bonding and dipolar interactions. The aim of this work was to add these dipolar interactions in addition of cubic and association contributions that were not ever done since typical CPA EOS only take account association by hydrogen bonding. This first paper is focused on the pure water and pure hydrogen sulfide. For pure H_2S, the parameters, such as dipole moment and size of the molecule, are fitted to experimental data along the saturation curve. The accuracy of the model, both for saturation pressure and liquid density, is much better as compared to previous cubic EOS. For pure H_2O system, the parameters are fitted along the saturation line of water. The accuracy is excellent along this coexistence curve for both saturation pressure and volumes of liquid and vapor. Parameters such as the energy of hydrogen bonding, dipolar moment and size of molecules are compatible with experimental data. In the temperature range of 25–400 °C and pressure range of 1–10,000 bar, the model predict satisfactorily the molar volume. This works opens the way to include other components such as gas and salts considering their energy contribution in the Helmholtz energy.

1. Introduction

Fluids are known to be efficient agents in mass and heat through the crust, especially in hydrothermal systems and also in the deep crust during metamorphism. They are known since a long time to be involved in mass transfer process by dissolution–precipitation reactions, devolatilization reactions in diagenesis (thermal maturation of organic matter, hydrocarbon cracking) to deep metamorphism (carbonate and hydroxyl-bearing minerals breakdown, reaction with graphite). Fluid mixing and unmixing processes during fluid percolation are common and have been often documented from isotope geochemistry and/or fluid inclusion data. Therefore, modeling the *P–V–T–X* properties is important for quantitative petrology and geochemistry as well as for the use of interpretation of paleo-fluid circulations studies based on fluid inclusions data. Equations of state are therefore the essential tool to model physical and chemical processes in which fluids are involved.

The equation state of the ideal gas $Z = \frac{Pv}{RT} = 1$ can be demonstrated using statistical thermodynamics with two hypotheses: dimensionless molecules and no molecular interaction potential. In a plot intermolecular potential versus distance between molecules, $V(r)$ is a straight line $V(r)=0$ from $r=0$ to ∞. The second and famous equation of state (EOS) of Van der Waals (1873) can also be derived using statistical thermodynamics with the following assumptions over the intermolecular potential: the molecules are treated as rigid spheres between which there is a small attractive interaction potential. The dependence of the potential can be of Sutherland type, square well potential. (Walton, 1976).

The Van der Waals (VdW) EOS is the mother of the cubic EOS with respect to volume and was the first to be compatible with the coexistence of vapor and liquid phases. Numerous equations deriving from the VdW EOS have been developed and also extensively used in the oil industries to model hydrocarbon fluids. The Redlich and Kwong (1949) EOS was modified from the VdW with a different attractive term, the repulsive term being the same. The Peng and Robinson (1976) EOS and the Soave–Redlich–Kwong (Soave, 1972) were also cubic EOS with different formulation of the attractive term and were popular in the oil industry in the thermodynamic modeling of hydrocarbon fluids. Due to the success of cubic EOS, there have been attempts to use cubic EOS to model aqueous fluids (*e.g.*, Holloway,

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1977, 1981; Bowers and Helgeson, 1983). However, the weakness of molecular interactions typical of Van der Waals interactions and intrinsic to cubic EOS was forgotten. A thorough review of cubic EOS is given by Duan and Hu (2004).

The Virial EOS is the second approach and is historically as old as the VdW EOS (Onnes, 1901). Its interpretation based on statistical mechanics is more recent (Ursell, 1927). The intractable N-body interaction problem is transformed into a soluble series of 1–body, 2–body, 3–body,… interaction problems which are quantitatively described by first, second, third, virial coefficient (Assael et al., 1996). However, it is worth noting that molecular interactions are assumed also to be weak, typical of gases at low and moderate densities, and modeled by pair potentials which are of hard sphere or Lennard–Jones types (Trusler, 2000). An extension of the virial EOS was done and by Benedict et al. (1940) in which an exponential term was introduced to compensate for the truncation of the virial series. A generalization of this equation was developed by Starling and Han (1972) and was very successful for pure substances and mixtures of hydrocarbons and gases. Duan and his collaborators, as well as many others, continued to develop this kind of EOS for modeling water, gases, water–gas mixtures, and water–gas–salt mixtures combining both molecular dynamics and fitting of experimental data. (*e.g.* Duan and Zhang, 2006; Duan et al., 1992; Duan et al., 1995a,b, 1996, 2000, 2003; Zhang and Duan, 2005).

Because of the difficulties of the problem, there were works which were dedicated to temperatures below 300 °C for water-rich fluids (with or without salts). In this temperature range, equilibrium between aqueous liquids and water-poor phase (either of liquid or vapor density) is frequently found either in sedimentary basins or till incipient greenschist metamorphic facies. Under these conditions, the contrasting compositions of phases (water-rich and water-poor) justified the use of dissymmetric models, one for each phase. This approach has been developed and was successful (Duan et. al., 1992; Duan and Mao, 2006; Dubessy et al., 2005). In such models, the water-poor phase or vapor phase could be modeled using a cubic EOS or a Virial derived EOS. The water-rich liquid phase was modeled using either the Pitzer model (Duan et. al., 1992; Duan and Mao, 2006) or extensions of Henry's law (Dubessy et al., 2005). Such approaches, although very useful below 300 °C, cannot be extended to higher temperatures. The need of a single model that applies to a wide range of *P–T–X* conditions remains a challenge in fluid geochemistry. One approach was the work of Duan et al. (1992). Duan et al. (1996) have used, for supercritical fluids and gases including water, an EOS for the vapor phase usually water-poor. This approach provided accurate results, but required many adjustable parameters which have very poor physical meaning excepted for two parameters which have physical meaning. Therefore, the aim of this work is to propose an equation of state with adjustable parameters that all have a physical meaning. The key to such models consists in taking into account the major type of interactions between the components.

Water is known to have forty five anomalies resulting from the hydrogen bonds between molecules (http://www.lsbu.ac.uk/water/). Hydrogen bonds are experimentally documented in a wide range of temperature at supercritical temperatures (*e.g.* Frantz et al., 1993; Hoffman and Conradi, 1997; Carey and Korenowski, 1998; Ikushima et al., 1998; Gorbaty and Kalinichev, 1995; Kalynichev and Churakov, 2001; Nakahara et al., 2001; Wernet et al., 2005), even if the extension of the transient network of hydrogen bonds is much more limited than it is in the 0–250 °C range. Therefore, the construction of an EOS for water requires taking into account the association between water molecules by hydrogen bonds. Such models were published since the nineties and are mainly represented by the SAFT (Statistical Association Fluid Theory, Chapman et al., 1990) equation of state and some simplified models named CPA (Cubic Plus Association, Kontogeorgis et al., 1996). Other strong molecular interactions are dipole–dipole interactions, which must be also included in the Helmholtz energy. The aim of this paper, and its companion paper, focuses on the formulation of an EOS which models the *P–V–T* properties of 1) a dipolar fluid like H_2S for which the liquid phase is not an associated liquid, and 2) a system like H_2O, whose liquid phase is an associated one by hydrogen bonding. In the second paper, mixtures of H_2O with H_2S, CH_4 and CO_2 will be considered.

2. Theory

2.1. The structure of the CPA–MSA model

Pressure derives from the Helmholtz energy (A) equation:

$$P = -\left(\frac{\partial A(T,V,N)}{\partial V}\right)_{T,N} \tag{1}$$

The Helmholtz energy is related to the canonical partition function Z by equation:

$$A(T,V,N) = -kT \ \ln\ (Z(T,V,N)) \tag{2}$$

A dipolar fluid can be considered as a fluid with two kinds of interactions, i.e. dipolar interactions and Van der Waals type molecular forces. If we assume these interactions to be independent, the partition canonical function can be written as product of two terms: one describing Van der Waals interactions $Z(T,V,N)^{\mathrm{VdW}}$ and one describing dipolar interactions, $Z(T,V,N)^{\mathrm{dd}}$. Therefore Eq. (2) transforms into Eq. (3):

$$\begin{aligned} A(T,V,N) &= -kT \ \ln\left(Z(T,V,N)^{\mathrm{VdW}} \times Z(T,V,N)^{\mathrm{dd}}\right) \\ A(T,V,N) &= -kT \ \ln\left(Z(T,V,N)^{\mathrm{VdW}}\right) - kT \ \ln\left(Z(T,V,N)^{\mathrm{dd}}\right) \end{aligned} \tag{3}$$

Each term can be regarded as the contribution of each type of interaction to the Helmholtz energy:

$$A(T,V,N) = A(T,V,N)^{\mathrm{VdW}} + A(T,V,N)^{\mathrm{dd}} \tag{4}$$

If another type of interaction occurs between molecules, such as association through hydrogen bonding as in water, the Helmholtz energy can be written following the same route:

$$A(T,V,N) = A(T,V,N)^{\mathrm{VdW}} + A(T,V,N)^{\mathrm{dd}} + A(T,V,N)^{\mathrm{association}} \tag{5}$$

Water was previously modeled by considering only association between water molecules with CPA equations (Kontogeorgis et al., 1996). However, hydrogen bonds break with increasing temperature. Therefore, at a constant liquid density, dipole–dipole interactions will be more important at high temperatures than at low temperatures. This justifies dipolar contribution in the model.

2.2. The reference fluid

The Van der Waals interactions corresponding to the reference fluid are described by a cubic equation of state, here the Soave–Redlich–Kwong equation of sate (Soave, 1972). The Helmholtz energy is given by Eq. (6):

$$A(T,V,N)^{\mathrm{SRK}} = -\ \ln\ (v-b) - \frac{a(T)}{bRT}\ \ln\left(\frac{v+b}{v}\right) \tag{6}$$

where the attractive parameter a is a function of reduced temperature and the acentric factor of the considered component:

$$a(T) = a_0\left[1 + c\left(1 - \sqrt{T/T_c}\right)\right]^2 \quad c = 0.48508 + 1.55171\omega - 0.15613\omega^2 \tag{7}$$

Parameters a_0 and b for SRK are related to critical parameters by Eq. (8):

$$a_0 = 0.42747\frac{(RT_c)^2}{P_c} \quad b = 0.08664\frac{RT_c}{P_c} \tag{8}$$

In this work, energetic contributions such as dipolar interactions and association, as well as VdW interactions, are taken into account separately.

Van der Waals theory is based on the assumption of a mean spherical potential which is not compatible with heterogeneities in vicinity of the critical point. Thus, the model is not suitable for accurate modeling of the critical point.

The a and b parameters for the reference fluid and the parameters of the other energetic contributions in the whole model are fitted from experimental data. Consequently, the pseudo-critical pressure and temperature (P_c* and T_c*) deduced from the a and b parameters (Eq. (9)), are different from the true critical parameters of the considered fluid.

$$a_0 = 0.42747\frac{(RT_c^*)^2}{P_c^*} \quad b = 0.08664\frac{RT_c}{P_c} \tag{9}$$

Acentric factor is related to the shape of the molecule and implicitly taken into account in dipolar moment and association terms of the SRK EOS (Soave, 1972): acentric factor of water molecule has a high value (0.344, Assael et al., 1996), whereas acentric factor of rare gases is close to zero since rare gases are spherical and simple monoatomic molecules without dipolar interaction and association. If only VdW interactions occurs between molecules of reference fluid, the reference fluid can be assumed to be typical of rare gas, thus, the acentric factor of reference fluid is taken equal to zero in the CPAMSA model.

2.3. Dipolar interactions

The dipolar interactions are modeled using the Padé approximant (Stell et al., 1972; Gubbins and Twu, 1978; Anderko and Pitzer 1993; Liu et al., 2005; and Gao et al. (1999) of the non-primitive MSA theory and perturbation theory. It is recalled in Eq. (10).

$$\begin{aligned} A^{dd} &= \frac{A_2^{dd}}{1-\frac{A_3^{dd}}{A_2^{dd}}} \quad \text{where} \\ \frac{A_2^{dd}}{RT} &= -\frac{2\pi}{3d^3}\rho\left(\frac{x_{dip}\mu^2}{kT(4\pi\varepsilon_0)}\right)^2 I_{dd} \\ \frac{A_3^{ddd}}{RT} &= \frac{4\pi^2}{27d^3}\rho^2\left(\frac{x_{dip}\cdot\mu^2}{kT(4\pi\varepsilon_0)}\right)^3 I_{ddd} \end{aligned} \tag{10}$$

$$\text{with} \quad \begin{aligned} I_{dd} &= \left(\frac{1}{3}\right)\frac{1+0.18158\rho^* - 0.11467\rho^{*2}}{1-0.49303\rho^* + 0.06293\rho^{*2}} \\ I_{ddd} &= \left(\frac{5}{24}\right)\frac{1+1.12754\rho^* + 0.56192\rho^{*2}}{1-0.05495\rho^* + 0.13332\rho^{*2}} \end{aligned} \tag{11}$$

$$\text{and} \quad \rho^* = \rho\cdot x_d\cdot d^3, \quad \rho = N_A/v \tag{12}$$

where 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). x_{dip} is the mole fraction of dipolar moment μ: for a pure H_2S sulfide fluid, x_{dip}=1 whereas, for a pure H_2O fluid, x_{dip} is the mole fraction of non-hydrogen bonded molecule.

2.4. The association between water molecules

Modeling of association started with Wertheim's works (Wertheim, 1984a,b, 1986). Chapman et al. (1990) derived the Statistical Association Fluid Theory (SAFT) to model associated fluids such as water, alcohols, acetic acid. The Helmholtz energy corresponding to the association between molecules is given by Eq. (13) for one site of association per molecules:

$$\frac{A^{assoc}}{RT} = \ln\left(X_{nb}\right) - \frac{X_{nb}}{2} + \frac{1}{2} \tag{13}$$

where X_{nb} is the mole fraction of non-bonded hydrogen molecules. X_{nb} is calculated from the association strength of hydrogen bonding Δ_{hb} according to Eq. (14):

$$X_{nb} = \frac{-1+\sqrt{1+4\rho\Delta_{hb}}}{2\rho\Delta_{hb}} \tag{14}$$

This association strength between two hydrogen bonded molecules 1 and 2 is a function of the product of the correlation function between the two molecules (g_{12}), the pair potential between the molecules which appears in the Mayer function (f_{hb}=exp(−$\beta\phi_{hb}$)−1) integrated over all the distances between molecules 1 and 2:

$$\Delta_{HB}^{12} = \int g_{12} f_{hb} d(2) \tag{15}$$

However, several molecules have more than one association site. For instance, water has four possible association sites as a consequence of its molecular electronic structure: two on the oxygen atom with the alone electron pair and on each hydrogen atom (Yakoumis et al., 1998).

According to Wertheim's theory, the Helmholtz association energy for M sites is the following:

$$\frac{A^{assoc}}{RT} = \sum_A\left[\ln\left(X_{nb}^A\right) - \frac{X_{nb}^A}{2}\right] + \frac{1}{2}(M) \tag{16}$$

with X_{nb}^A is the mole fraction of non-hydrogen bonded molecule to any site A, and M the number of sites (M=4 in our case), summation being done over all association sites. Chapman et al. (1990) derived the mole fraction of non-bonded molecules at site A Eq. (17) and recalled by many other authors (Huang and Radosz, 1990) and the association strength Δ_{hb}^{AB} Eq. (18):

$$X_{nb}^A = \left(1+\rho N_{Av}\sum_B X_{nb}^B \Delta_{hb}^{AB}\right)^{-1} \tag{17}$$

with the summation done over all association sites

$$\Delta_{hb}^{AB} = g_{12}\left[\exp\left(\varepsilon_{hb}^{AB}/kT\right) - 1\right]\cdot(\beta b) \tag{18}$$

with g_{12} the correlation function (19), ε_{hb}^{AB}, 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 assigned in the SAFT model to the interaction volume between two sites of association but considered as an adjustable parameter. The correlation function is calculated on the model of the correlation function of hard-spheres (Kontogeorgis et al., 1996):

$$g_{12} = \frac{2-\frac{b}{4v}}{2\left(1-\frac{b}{4v}\right)^3} \tag{19}$$

Eq. (17) can be solved for water. It is considered here four association sites: two association sites A and B on oxygen atom and one association site on each hydrogen atom defining sites C and D. As

Table 1
Values of the parameters obtained for H_2S fitting the model. T_c* and P_c* are pseudo-critical temperature and pressure of the reference fluid modeled by SRK EOS

T_c* (K)	P_c* (bar)	a (J m^3)	b (cm^3 mol^{-1})	μ_{mod} (D)	μ_{exp} (D)	d_{mod} (Å)	d_{exp} (Å)
330.2	82.0	0.3929	29.01	1.11	0.97–1.134	2.50	2.6–2.7

Subscripts mod and exp indicate respectively values of the model and the experimental one. μ: dipolar moment of H_2S molecule; d: diameter of H_2S molecule.

hydrogen bonding exists only between O and H atoms of two distinct molecules, the following relationships stand for strength association:

$$\begin{aligned} &\Delta_{hb}^{AA} = \Delta_{hb}^{AB} = \Delta_{hb}^{BB} = \Delta_{hb}^{CC} = \Delta_{hb}^{CD} = \Delta_{hb}^{DD} = 0 \\ &\Delta_{hb}^{AC} = \Delta_{hb}^{AD} = \Delta_{hb}^{BC} = \Delta_{hb}^{CD} = \Delta_{hb} \end{aligned} \quad (20)$$

The mole fraction of each type of molecules non-bonded at a given site is equal and given by equations given by Huang and Radosz (1990):

$$X_{nb}^{A} = X_{nb}^{B} = X_{nb}^{C} = X_{nb}^{d} = \frac{-1+\sqrt{1+8\rho\Delta_{hb}}}{4\rho\Delta_{hb}} \quad (21)$$

As temperature increases, hydrogen bonds break which reflects in the increase of non-hydrogen bonded molecules of water which are dipolar. Thus, in the case of water, it is necessary to estimate the number of dipole moments. For one given site, for instance A, there are four types of molecules: the quadrimers, and the three m-mers non-bonded with site A, m=1 to 3. With respect to site A, X_{hb}^{A} is the mole fraction of these molecule aggregates minus the quadrimers. The quadrimers can be assumed to have a tetrahedral symmetry like in ice and therefore the dipolar moment can be approximated to zero. Therefore, X_{nb}^{A} is the mole fraction of aggregates with non-zero dipole moments with respect to site A.

3. The fitting procedure

Equation of state is written as form of Helmholtz energy. All calculations are made with the algorithm LOTHER (Thiéry, 1996). It is an object-oriented library written in C++ and containing a number of routines that facilitate thermodynamic calculation. With LOTHER, the Helmholtz energy is thus differentiated analytically up to the fourth order with respect to the temperature, pressure and composition. Furthermore, the LOTHER software allows fitting procedures by varying values of equation of state parameters during thermodynamics properties calculations.

Optimizations are performed along vapor–liquid equilibrium on experimental saturation pressures and liquid densities at equilibrium from boiling temperature to critical temperature of the pure components studied. Thus optimization procedures consist to minimize the objective function Eq. (22). Optimization is not carried out on

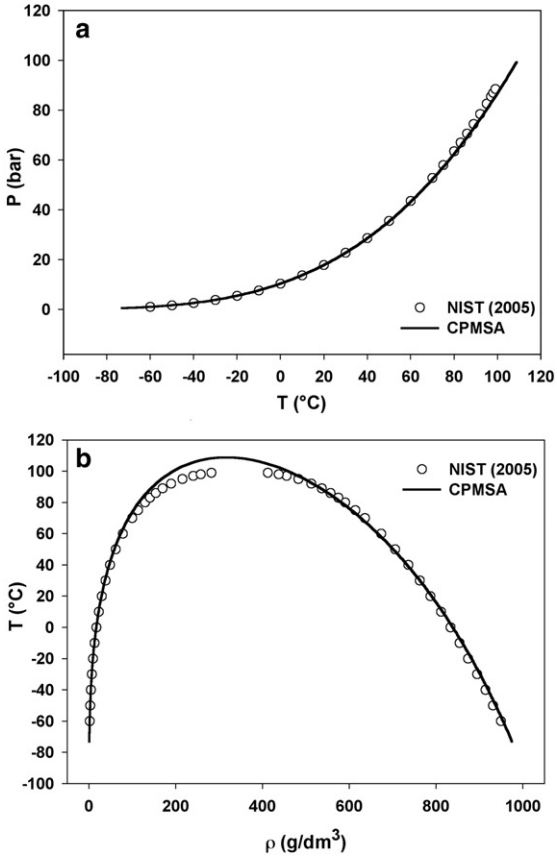

Fig. 1. Comparison of calculated P–v–T properties of hydrogen sulfide with reference data (NIST, 2005). (a) saturation pressure; (b) density along VLE.

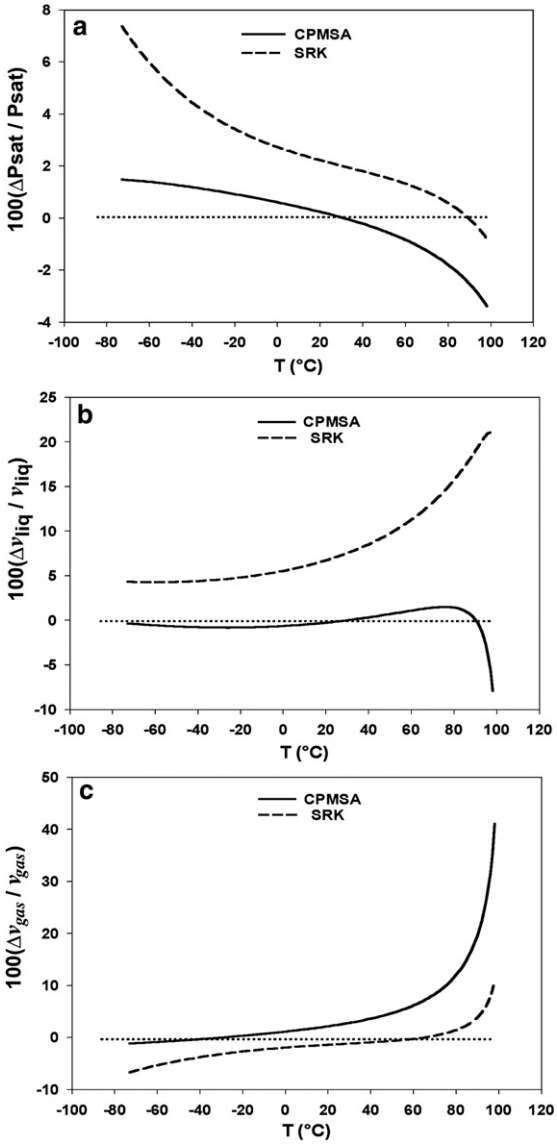

Fig. 2. Error in percent of the modeling of hydrogen sulfide: (a) saturation pressure, (b) volume of the liquid phase,(c) volume of the vapor phase along the coexistence curve calculated with SRK model, and this model (CPMSA).

Table 2
Standard deviation of SRK and this model along the saturation curve of hydrogen sulfide

EOS	$\sigma(V_{liq}/V_{liq})$	$\sigma(V_{gas}/V_{gas})$	$\sigma(P_{sat}/P_{sat})$
SRK	0.082	0.026	0.028
CPMSA	0.008	0.046	0.010

Table 4
Comparison of the pseudo-critical values of the reference fluid of water (H_2O^*) with critical points of Ne and Ar rare gases

	H_2O^*	Ne	Ar
P_c (bar)	34.07	27.6	48.7
T_c (K)	65.5	44.4	150.8

the volumes of vapor phase in view to focus on the accuracy of representation of the liquid phase.

The objective function is as follow:

$$\text{Fobj} = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{\text{Psat}_i^{\text{calc}} - \text{Psat}_i^{\text{exp}}}{\text{Psat}_i^{\text{exp}}}\right)^2 + \frac{1}{n}\sum_{i=1}^{n}\left(\frac{\text{Vliq}_i^{\text{calc}} - \text{Vliq}_i^{\text{exp}}}{\text{Vliq}_i^{\text{exp}}}\right)^2 \quad (22)$$

For one pure component, this objective function is calculated for each combination of all parameters whose matrix respects the three following points: (1) pseudo-critical parameters (T_c* and P_c*) are taken between 1 K and experimental T_c, and between 1 bar and experimental P_c. Parameters a_0 and b are then calculated from T_c* and P_c*. (2) Values of physical parameters (ε_{hb}^{AB}, d, μ) are refined close to their experimental values. (3) β is tested between 10^{-4} and 1.

Combination of parameters which minimize the objective function is thus retained.

Fugacities are calculated from LOTHER with expression given in the Appendix.

4. Experimental data base

Experimental data along the coexistence curve of pure H_2S are issued from Reamer et al. (1950), Clark and Glew (1970) and Cubitt et al. (1987). Those experimental data are consistent from triple point to critical point with the NIST Standard Reference Database 69 (2005) which gives an accurate model for thermodynamics properties of hydrogen sulfide from data reviewed by Sadoka and Uematsu (2004). The uncertainties of the NIST model in density are 0.1% in the liquid phase below the critical temperature, 0.4% in the vapor phase. Optimization of the CPMSA model for hydrogen sulfide is thus made on data given by NIST for pure H_2S.

All PVT data of water come from NIST-Steam (Harvey et al., 1996) which uses algorithm adopted by International Association of Water and Steam (IAPWS).

5. Results and discussion

5.1. Hydrogen sulfide

The following four parameters of the model CPMSA (Cubic+MSA) were fitted: the a and b parameters of the SRK EOS relative to the reference fluid, the dipolar moment and the size of the molecules. The acentric factor was constrained to be zero. Values of the parameters obtained after fitting are given in Table 1 and the diameter of molecule and dipolar moment of the model are compared with experimental data. Value of the dipolar moment is coherent with the range of experimental data (Henon et al., 2003; Nath, 2003). The diameter of the molecule is also slightly lower than experimental data: d=2.50 Å instead of 2.6 Å. The pseudo-critical temperature and pressure of the reference fluid modeled by the SRK EOS are lower than the true critical points. However, the critical point is slightly overestimated both in temperature and pressure: 379 K instead of 373 K and 100 bar instead of 89.4 bar. This overestimation of the values of the critical temperature and pressure is consistent with the fact that such physical based model does not take into account the fluctuation densities and their spatial correlation. Fig. 1a is a plot of the saturation pressure versus temperature. Fig. 1b is a plot of the density of the coexisting liquid and vapor phases versus temperature. Experimental saturation pressure data are reproduced with very good accuracy better than 0.1% on average. From the triple point to a reduced temperature T_r=0.986 (T=368 K), the average error on the molar volume of the liquid is less than 1.0% (Fig. 2c). For the vapor phase, the accuracy is slightly less good that for the liquid, but it is better than 5% (on average) from triple point to a reduced temperature T_r=0.97 (T=363 K), probably because the objective function is not optimized on the vapor volumes. Statistical analysis shows the present model is much better than SRK EOS and shows that dipolar interaction is the main molecular interaction and is satisfactorily taken into account by the model. Average statistical deviations of the CPMSA model are given in Table 2 and are compared to these obtained with SRK.

Table 3
Values of the parameters obtained from fitting the CPAMSA model for water

a (J m^3)	b (m^3 mol^{-1})	μ (D)	d (Å)	ε_{hb}^{AB}/k (K)	β
0.0871	13.851 1E−6	2.2	3.2	2496	0.026

5.2. Water

Six parameters are determined: the energy of hydrogen bond (ε_{hb}), the dipolar moment of the water molecule (μ), the diameter of the

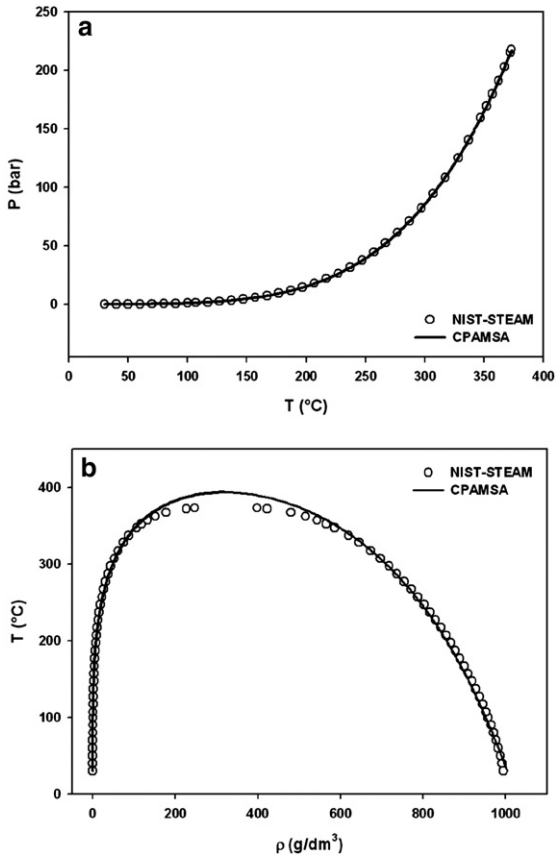

Fig. 3. Comparison of calculated P–v–T properties of water with experimental data (NIST-Steam). (a) saturation pressure; (b) density along VLE.

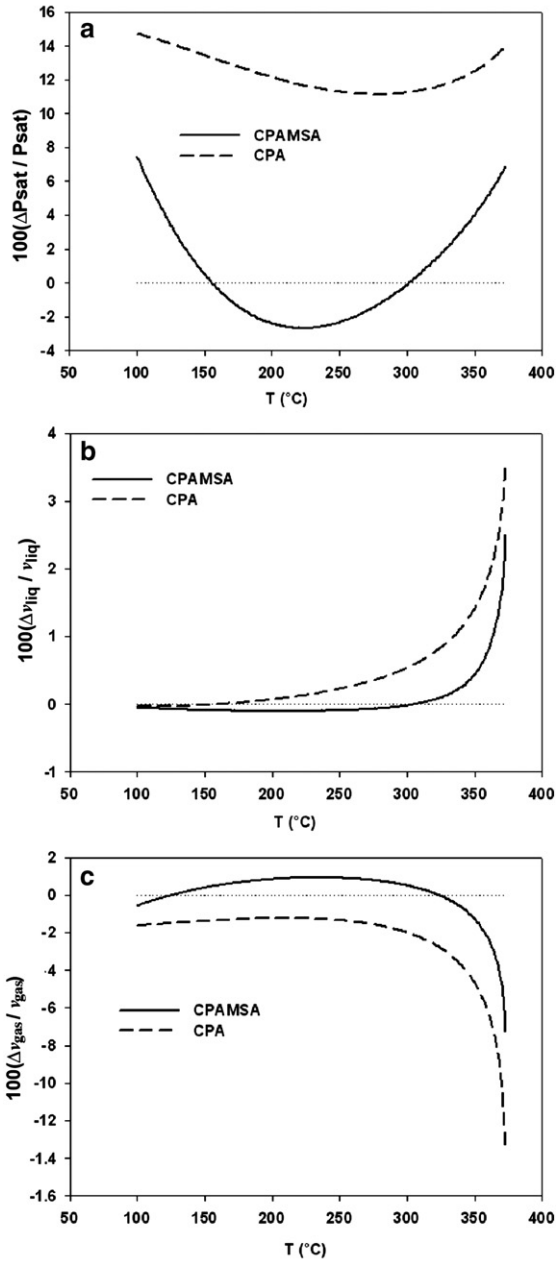

Fig. 4. Error in percent of the modeling of water: (a) saturation pressure, (b) volume of the liquid phase,(c) volume of the vapor phase along the coexistence curve calculated with CPA models, and this model (CPAMSA).

molecule (d), the a and b parameters of the SRK EOS corresponding to the reference fluid, and the association volume (β). The acentric factor is considered to be zero like for hydrogen sulfide. The dipolar moment of the water molecules is known to vary with the association degree of the water molecules. The value of the dipolar moment is 1.8 D for isolated water molecules representative of water in low density vapor phase whereas it is around 2.7 D in the dense liquid phase at room temperature (Silvestrelli and Parrinello, 1999). In order to maintain

Table 5
Standard deviation of SRK, CPA and this model along the saturation curve of water

EOS	$\sigma(V_{liq}/V_{liq})$	$\sigma(V_{gas}/V_{gas})$	$\sigma(P_{sat}/P_{sat})$
SRK	0.4161	0.097	0.032
CPA	0.058	0.266	0.125
CPAMSA	0.033	0.121	0.030

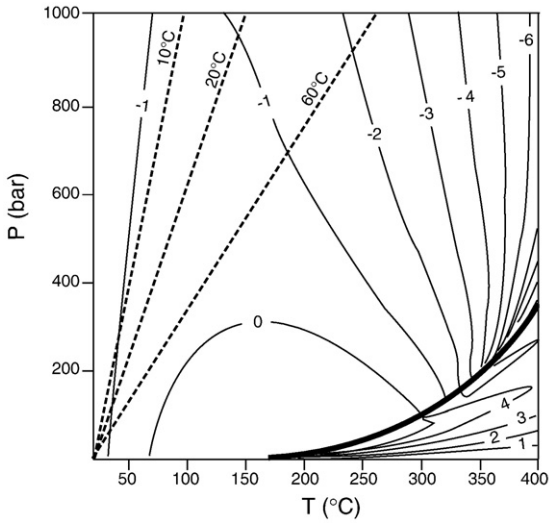

Fig. 5. Mapping of errors of the molar volume of water in the P–T plane to 1000 bar.

the symmetry of the model, a single value of 2.2 D has been chosen for the dipole moment of water molecules. The diameter of the molecule modeled as a hard sphere molecule is 3.2 Å. The ε value of hydrogen bond is constrained to vary in the interval range $20 < \varepsilon_{hb} < 22$(kJ·mol^{-1}). Values of parameters are given in Table 3.

The pseudo-critical temperature and pressure of the Van der Waals fluids associated with this model are well below the true critical temperature and pressure (Table 4) and are between the values of critical points of Ne and Ar rare gases. The model overestimates slightly the critical point of water since the model predictions are 394 °C–275 bar to be compared with the experimental values (373 °C–221 bar). The accuracy of the saturation pressure is better than 0.1% up to 360 °C, which is a reduced temperature of 0.98. It is worth noting also the critical pressure and temperature are better than values predicted by the CPA model that are respectively 410 °C and 304 bar.

Pressure and density of the liquid–vapor coexisting curve are correctly modeled as shown in Fig. 3. Fig. 3b shows the overestimation of the critical zone. Errors of the model are given in Fig. 4. The model fits P–v–T experimental data better than the CPA model as shown by the statistical parameters (Table 5).

A mapping of errors on the molar volumes has been done in the 25–400 °C and 1–1000 bar pressure–temperature range (Fig. 5) and up to 10000 bar (Fig. 6). Three lithostatic gradients plotted in this volume

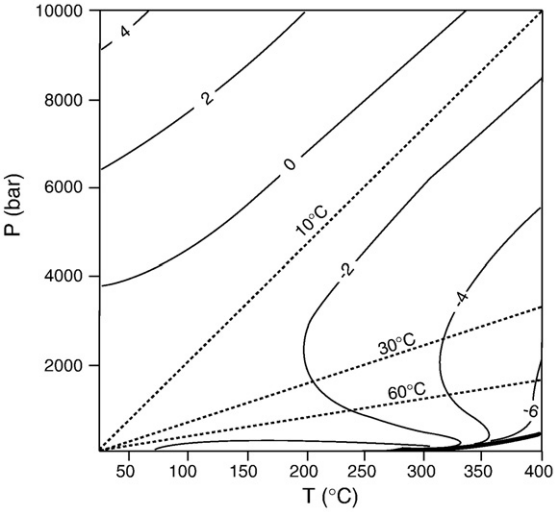

Fig. 6. Mapping of errors of the molar volume of water in the P–T plane to 10,000 bar.

error cartography plane show the good quality of the model for geologic conditions since the error on the volume are smaller than 2%. The model is not good near the critical region above 360 °C, and along the extrapolation of the saturation curve above critical temperature in the *P*–*T* plane. The model degrades above 325 °C and for pressures between 600 and 1000 bar.

Above the critical point, the model has been fitted along a curve which is the extrapolation of the saturation curve in the *P*–*T* plane. Errors on the volumes above 400 °C may reach 14–16% for pressures between 1000 and 2000 bar, indicating this model is not relevant for supercritical temperatures.

6. Conclusion

An equation of state to model *L*–*V* equilibria of H_2O and H_2S systems is proposed. The Helmholtz energy of studied fluids has been written as the sum of different energetic contributions by factorization of partition function. The model developed here for the pure H_2O and H_2S considers three contributions. The first contribution represents the reference Van der Waals fluid which is modeled by the SRK cubic EOS. The second contribution accounts for association through hydrogen bonding and is modeled by a term derived from Cubic Plus Association (CPA) theory. The third contribution corresponds to the dipolar interactions and is modeled by the Mean Spherical Approximation (MSA) theory. The resulting CPAMSA equation has six adjustable parameters, three of which represent physical terms whose values are close to their experimental counterpart. This equation results in a better reproduction of the *P*–*V*–*T* properties of pure water than these obtained using the classical CPA equation along the vapor–liquid equilibrium. Similarly, taking into account dipolar interactions, together with the SRK cubic equation of state for calculating molar volume of H_2S as a function of pressure and temperature, results in a significant improvement compared to the SRK equation alone. This model improves significantly the calculation of molar volume.

Results obtained with CPAMSA on pure components open the way of modeling realistic geological fluids (i.e. multicomponents fluids) as it will shown in the next paper on H2O–H_2S, H_2O–CO_2 binary systems (Perfetti et al., in prep). Thus CPAMSA model should be used as well for fluid inclusions studies which involved many gases and water, as calculations within fluid–rocks interaction software.

7. 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 = $6.02205 \cdot 10^{23}$ (mol^{-1})
R	gas constant = 8.3144 (J K^{-1} mol^{-1})
k	Boltzmann constant: $1.38066 \cdot 10^{-23}$(J K^{-1})
ε_0	vacuum permittivity: $8.854188 \cdot 10^{-12}$ (J C^{-2} m^{-1})
$4\pi\varepsilon_0$	$1.112650 \cdot 10^{-10}$ (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}]
$\rho = N_{Av}/v$	number density (m^{-3})
d	diameter of a molecule (m); [Å]
μ	dipole moment (C m^{-1}); [D]
ε_{hb}^{AB}	energy of hydrogen bond between A and B sites (J mol^{-1});
g_{12}	radial distribution function
β	interaction volume

Appendix A. Derivation of the fugacity from a volume-explicit equation of state

Common equations of state are based on a function of temperature (T), molar volume (V) and mole fraction (x_i), as they are formulated by means of an expression of the Helmholtz free energy $A(T, V, x_i)$ or of the pressure $P(T, V, x_i)$. However, classical books give usually expressions of thermodynamic properties in terms of T, x_i and pressure (P). As it is preferable and easier to work in the natural set of variables (T, V, x_i), the calculation formulas are given here for the fugacity f_i and fugacity coefficient φ_i in a mixture of n components in the space of variables (T, V, x_i).

The fugacity expresses the departure of the chemical potential difference ($\mu_i - \mu_i^*$) in an isothermal compression from a very expanded state (state 1, $V_1 = \infty$, $P_1 = 0$) to a compressed state (state 2, $V_2 = v$, $P_2 = P$). μ_i^* is the chemical potential of component i in an ideal gas, and in what follows, all asterisked parameters refer to properties of the perfect ideal gas. During a small compression step, we have:

$$\begin{aligned} RTd\ \ln\ (\varphi_i) &= RTd\ \ln\ (f_i) - RTd\ \ln\ (P) \\ &= d\left(\mu_i - \mu_i^*\right) - RTd\ \ln\ (P) \\ &= d\left(a_i + PV - a_i^* - RT\right) - RTd\ \ln\ (P) \\ &= d\left(a_i - a_i^*\right) + d(PV - RT) - RTd\ \ln\ (P) \end{aligned} \tag{A1}$$

which lead to:

$$d\ \ln\ (\varphi_i) = d\ \ln\left(\frac{a - a_i^*}{RT}\right) + d\ \ln\ (Z - 1) - d\ \ln\ (Z) \tag{A2}$$

where Z is the compressibility factor defined by $Z = PV/RT$, and a_i is the partial Helmholtz free energy of i. This latter quantity a_i in a mixture of N components is obtained from the Helmholtz free energy by:

$$a_i = \left(\frac{\partial(nA)}{\partial n_i}\right)_{T,V,n_j} \tag{A3}$$

where n_i is the number of moles of component i, and n is the total number of moles of the mixture. Thus,

$$\begin{aligned} \left(a_i - a_i^*\right) &= \left(A - A^*\right) + \left(\frac{\partial\left(A - A^*\right)}{\partial n_i}\right)_{T,V,n_j} \\ &= \left(A - A^*\right) + \left(\frac{\partial\left(A - A^*\right)}{\partial x_i}\right)_{T,V,x_j,j\neq i} - \sum_{j=1}^{N} x_j \left(\frac{\partial\left(A - A^*\right)}{\partial xj}\right)_{T,V,x_j} \end{aligned} \tag{A4}$$

For the ideal gas,

$$a_i^* = RT\ \ln\ (v) + a_i^o(T, x) \tag{A5}$$

where $a_i^o(T,x)$ is an integration constant, which depends only on the temperature and the composition. Let's introduce the reduced function, Y, defined by:

$$Y = \frac{a_i - a_i^*}{RT} \tag{A6}$$

As the $a_i^o(T,x)$ disappears in the difference ($a_i - a_i^*$), one obtains

$$Y = \frac{a_i}{RT} + RT\ \ln\ (v) \tag{A7}$$

By combining Eqs. (A2) and (A6), we get:

$$d\ \ln\ (\varphi_i) = d(Y) + d\ \ln\ (Z-1) - d\ \ln\ (Z) \tag{A8}$$

This function Y tends towards 0 when the fluid expands indefinitely:

$$\lim_{V\to\infty}(Y) = 0 \tag{A9}$$

and in the same way,

$$\lim_{V\to\infty}(Z) = 1 \tag{A10}$$

Therefore, by integration of $d\ln(\varphi_i)$ from $V_1=\infty$ to $V_2=V$, one obtains:

$$\begin{aligned}\ln\ (\varphi_i) &= Y + Z - 1 - \ln\ (Z)\\ &= \frac{a_i}{RT} + \ln\ (v) + Z - 1 - \ln\ (Z)\end{aligned} \tag{A11}$$

From the definition equation $f_i = x_i\varphi_i P$, one gets

$$\begin{aligned}f_i &= x_i\frac{P}{Z}\ \exp\left(\frac{a_i}{RT}+Z-1\right)\\ &= x_i RT\ \exp\left(\frac{a_i}{RT}+Z-1\right)\end{aligned} \tag{A12}$$

In the case of a pure fluid, the equation simplifies to:

$$f = RT\ \exp\left(\frac{A}{RT}+Z-1\right) \tag{A13}$$

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