Modeling Phase Equilibria for Acid Gas Mixtures Using the CPA Equation of State. I. Mixtures with H_2S

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The Cubic-Plus-Association (CPA) equation of state is applied to a large variety of mixtures containing H_2S, which are of interest in the oil and gas industry. Binary H_2S mixtures with alkanes, CO_2, water, methanol, and glycols are first considered. The interactions of H_2S with polar compounds (water, methanol, and glycols) are modeled assuming presence or not of cross-association interactions. Such interactions are accounted for using either a combining rule or a cross-solvation energy obtained from spectroscopic data. Using the parameters obtained from the binary systems, one ternary and three quaternary mixtures are considered. It is shown that overall excellent correlation for binary mixtures and satisfactory prediction results for multicomponent systems are obtained. There are significant differences between the various modeling approaches and the best results are obtained when cross association is explicitly accounted for, especially using the cross-association energy from independent experimental studies rather than from combining rules. © 2010 American Institute of Chemical Engineers *AIChE J,* 56: 2965–2982, 2010

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Importance of H_2S in Oil and Gas Industry

Phase equilibria of mixtures containing acid gases like CO_2 and H_2S with water, alcohols, and glycols are of great importance in numerous processes in the oil and gas and chemical industries. Water, typically found in petroleum reservoirs or brine may cause reduction of the amount of gas available for mixing with hydrocarbons and this effect increases with pressure and the amount of the aqueous phase (while it decreases with salinity). Understanding of the phase behavior of gas (methane, H_2S, and CO_2)/water (brine)/oil is of importance for the design of these processes.

In particular, H_2S is an important nonhydrocarbon component of petroleum. Carroll and Mather stated more than 10 years ago that refiners will have in the future to process feed stocks that are heavier (contain larger hydrocarbons) and sourer (contain more sulfur compounds, including hydrogen sulfide) than in the past.[1] Indeed, this is the case already today. Modeling the production and processing of these sour, heavy crude substances, requires accurate vapor-liquid equilibrium data. Only few data exist due to especially the corrosion and toxicity of H_2S, combined also with the high pressures involved with several applications.

Moreover, processing of natural fluids with significant amount of H_2S is increasing as search and effort for more effective use of energy resources increase. Related problems of practical interest are the processing of sour natural gas to enhance ethane and propane recovery, the sweetening of liquefied petroleum gases (LPG), which are often contaminated with H_2S and/or CO_2 (components which must be removed from LPG).[2] Moreover, there is renewed interest in developing oil and gas reserves, which have been bypassed

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previously because of high content of CO_2 and H_2S. In addition, a number of rich H_2S sour natural gas or oil fields have been discovered around the world, e.g., North China, Canada, Italy, and Greece (where the "Prinos" reservoir oil is with about 42% (mole) H_2S).[2] Some of these fields are already under production. Refiners already face declining crude oil quality as they have to process feedstocks that become heavier and sourer than in the past.

Thermodynamic data for H_2S containing mixtures (with hydrocarbons, water, and other polar chemicals) are needed in numerous processes, e.g., gas processing, refining, and reinjection of acid gases in deep reservoirs.

With respect to gas processing, in the petroleum industry, H_2S (and CO_2) acid gases are generally removed from natural gas/gas streams by absorption/stripping process. The solvent is often an aqueous solution of alkanolamines especially MEA, DEA, and MDEA. MDEA is particularly suitable for H_2S due to rapid reaction with H_2S and low heat of absorption and lower corrosivity, which leads to lower energy requirements for regeneration, and selective removal of H_2S from process streams containing CO_2 as well (due to slower reaction with CO_2). Mixed solvents (MDEA together with physical solvents like sulfolane and methanol) receive increasing interest. Improved design of gas treating processes requires VLE data for CO_2-H_2S-water-alkanolamine-possible physical solvent mixtures. The importance of gas processing is expected to increase in the next few decades, but future developments will depend on the progress of gas processing technologies to give access to reserves now not exploitable. More than 30% of the available gas fields are acid, containing large quantities of CO_2 and H_2S and other sulfur compounds.[3]

Finally, Ungerer et al. discuss two more aspects where extensive thermodynamic data for H_2S-containing mixtures is needed.[4] First, the reinjection of acid gases in deep reservoirs is mentioned. To improve the economics of producing H_2S-rich gas fields, one option that is considered is to reinject H_2S in deep reservoir rocks, instead of converting it into sulfur. In these reservoirs, H_2S may contact oil deposits under high pressures. Design of such reinjection processes requires extensive data about phase equilibrium, volumetric and transport properties of H_2S-hydrocarbon mixtures.[4] Another important application is related to refining. Hydrotreating is an important process for the processing of heavy crude oils as it allows cracking of heavy compounds with generation of excessive amounts of coke, because of the use of high-pressure hydrogen. Hydrotreating processes are also used to remove sulfur-bearing compounds such as thiols and thiophene derivatives. Sulfur is then converted into H_2S, which is distributed between the liquid and vapor phases. Design of such units requires phase equilibrium data at typical process temperatures (430°C), which are often above the investigated range of temperatures with conventional models. Heavy hydrocarbons are unstable at these high temperatures.

The purpose of this work is to present, using an association equation of state (the CPA model), an extensive modeling study of the phase behavior of H_2S-containing systems with various compounds (hydrocarbons, CO_2, methanol, water, and glycols). As a central characteristic of models like CPA is the implementation of the different types of cross interactions, the nature of H_2S and especially its cross interactions with polar compounds is discussed next. In the next section are also briefly discussed previous modeling attempts for H_2S-containing systems. Then, the CPA equation of state is presented in short together with the modeling approaches and the pure parameters obtained with the various methods. Results for binary mixtures are presented and discussed. Next, the predictions for one ternary and three quaternary mixtures are presented and discussed. Conclusions and recommendations are summarized in the last section.

The Nature of H_2S and its Interactions with Polar Chemicals—Literature Studies on Thermodynamics of H_2S Containing Mixtures

Hydrogen sulfide is usually considered as a nonassociating compound. There is no experimental evidence for strong specific interactions between H_2S molecules. The absence of strong self-associating interactions is the main reason for the large difference between the physicochemical properties of H_2S and water, which is considered as a structural analog since sulfur and oxygen belong to the same group of the periodic table. This is illustrated in Table 1, where the physical properties of H_2S, other compounds considered in this work and some simple hydrocarbons are shown.

Despite this inert character, there are some studies about the interactions between H_2S molecules, especially in presence of polar compounds. Cabaleiro-Lago et al. studied the naphthalene-H_2S interactions using ab initio calculations.[5] They concluded that in H_2S clusters there is a low tendency for self-association. Naphthalene-H_2S-H_2S structures with no hydrogen bonds between H_2S molecules were at least as stable as the hydrogen bonded ones. Moreover, Pecul performed ab initio calculations to investigate H_2S-H_2S interactions.[6] He estimated the binding energy (due to the formation of a hydrogen bond) between two H_2S molecules to range between –3766 and –6276 J mol^{-1}. Compare this to a value about –25,000 J mol^{-1}, for a typical hydrogen bond. From the aforementioned studies, it is clear that only weak hydrogen bonding interactions may occur between H_2S molecules.

While self-associating interactions between H_2S molecules are very weak, H_2S can cross associate with other hydrogen bonding fluids. Sennikov et al. studied the intermolecular interactions of hydrogen sulfide with water using IR spectroscopy.[7] They concluded that weak complexes of water and H_2S molecules are formed in the liquid phase. They estimated the association energy equal to –10,878 J mol^{-1}. Furthermore, ab initio calculations showed that the most stable hydrogen bond between water and hydrogen sulfide is when the latter (H_2S) acts as a proton donor, while water acts as a proton acceptor.[8–10] A summary of the reported association energies for the H_2S-H_2O cross interactions is presented in Table 2.

On the other hand, relatively few studies exist for the cross interactions of H_2S with other hydrogen bonding fluids. Sennikov et al. performed an IR-spectroscopic study and report that a weak hydrogen bond is established between ethanol and H_2S in liquid phase.[11] They estimated the hydrogen bonding enthalpy to be equal to –8786 J mol^{-1}.

Table 1. Some Physical Properties of H_2S, Water, CO_2, Methanol, MEG, and Simple Hydrocarbons

Molecule	Molecular Weight (g mol^{-1})	Dipole Moment (D)	Quadrupole Moment (C m^2)	Polarizability (Å^3)	van der Waals Volume (cm^3 mol^{-1})	Boiling Point (K)
Methane	16.04	0		2.59	17.05	111.66
Ethane	30.07	0	−2.16	4.45	27.34	184.55
Propane	44.10	0.084		6.29	37.57	231.11
Butane	58.12	0		8.22	47.80	272.65
Ethylene	28.05	0	+4.98	4.25	23.88	169.41
CO_2	44.01	0	−14.3	2.91	19.70	194.70
H_2S	34.08	0.97		3.78	18.72	212.8
Water	18.02	1.85		1.45	12.37	373.15
Methanol	32.04	1.70		3.23	21.71	337.85
MEG	62.07	2.31			36.54	470.45

In conclusion, H_2S is shown to cross associate with both water and alcohols (especially methanol and ethanol) and the same can be said for CO_2-water and CO_2-alcohol mixtures, as will be discussed in the forthcoming article (Part II in this series).

Previous Studies with Association (and Other) Models for H_2S Systems

Compared to mixtures containing CO_2, relatively few studies have been published with association models for H_2S containing systems. Most of these previous investigations have been made with different versions of the CPA approach. More specifically, Ruffine et al. have used CPA (as presented here, see "The CPA Equation of State" section) for VLE of binary H_2S mixtures (with water, methanol, and alkanes).[12] Satisfactory results are obtained when H_2S is considered to be a self-associating molecule with three association sites. They have used as combining rules for the cross-associating parameters the geometric mean rule for the cross-association energy and the arithmetic mean rule for the cross-association volume, which is different than the CR-1 rule, presented in "The CPA Equation of State" section.

Kontogeorgis et al. have presented a few calculations for H_2S-water, H_2S-methanol, and H_2S-glycols.[13] It is illustrated that explicitly accounting for cross-association (solvation)—using the modified CR-1 rule, see "The CPA Equation of State" section—improves the VLE of H_2S-mixtures with water and methanol, while there is essentially no influence in the case of H_2S-glycol mixtures. The latter study has been further verified by the recent investing of Afzal et al. who made a systematic investigation of H_2S (and other compounds) with MEG, DEG, and TEG (Afzal et al., submitted for publication). A single (glycol-specific) temperature independent interaction parameter (in the region 298–398 K) is sufficient in all cases.

An alternative approach for modeling acid gas mixtures with a CPA-type EoS has been recently presented by Perfetti et al.[14,15] They developed a polar CPA EoS, based on a non-primitive mean spherical approximation (MSA) theory, with the polar term expressed via the Padé approximant and the integrals given by Gubbins and Twu.[16] Perfetti et al.[14,15] applied the polar CPA (termed CPAMSA) to water-H_2S, CO_2-water, and water-methane. Water is treated as both polar and associating compound (six pure compound parameters), H_2S is treated as polar nonassociating compound (four pure compound parameters), whereas methane and CO_2 are treated as "inert" (nonpolar, non–self-associating compounds) and have thus only three parameters (critical properties and acentric factors). For mixtures, mixing rules are needed for the dipole moment appearing in the MSA term. Some preliminary first results are promising (especially for the pure compounds) but improvements will be needed. For example there is need in the current version of CPAMSA for two different sets of interaction parameters for water-methane (for the liquid and gas phase), which are, moreover, temperature-dependent and have been correlated using a three-parameter correlation. The best results are obtained for water-H_2S for which the interaction parameters are also small, about 0.02 in the 60–180°C range (roughly temperature independent), while higher interaction parameter values are needed for water-CO_2, which are dependent on temperature as they vary from 0.05 (at 50°C) up to –0.2 (300°C). No results were presented with temperature-independent interaction parameters.

The most recent investigation is that of Li and Firoozabadi who modeled with a Peng Robinson CPA (PR-CPA) the multicomponent system water/methane/CO_2/H_2S (and the corresponding binaries).[17] They conclude that good results are obtained if the cross association (solvation) between acid gases but also methane with water is accounted for. They state that a certain degree of cross association, possible due to induced polar interactions, is present between water and methane or ethane at very high pressures.

Finally, relatively few of the "conventional" models, e.g., cubic equations of state have been extensively applied to H_2S systems. Most such models have been applied to mixtures of H_2S with hydrocarbons.[1,2,18,19] In these articles, interaction parameters (k_{ij}) for H_2S-hydrocarbons have been presented for cubic EoS (SRK and PR). Generalizations with the molecular weight and acentric factor have been also given. When cubic EoS is extended to H_2S-water, satisfactory VLE results can be obtained if two interaction parameters (corrections to the cross energy and covolume) are used

Table 2. Association Energies for the H_2S-H_2O Complex

Interaction	Association Energy (J mol^{-1})	Technique	References
$H_2O\cdots H_2S$	−13,807	Ab initio calculations	10
$HOH\cdots SH_2$	−12,552		
$HOH\cdots H_2S$	−10,878	IR (experimental)	7
$H_2O\cdots H_2S$	−6276	Ab initio calculations	8
$HOH\cdots SH_2$	−5439		

Table 3. Parameters for Pure Fluids (Obtained in This Work)

Association Scheme*	Temperature Range	a_0 (L^{2}bar mol^{-2})	b (L mol^{-1})	c_1	ε (bar L mol^{-1})	β	%AAD† in P^{sat}	%AAD† in ρ^{liq}
H_2S								
n.a.	T_{melt}–0.9 T_{cr}	4.45050	0.0285	0.60265	–	–	0.4	1.4
2B	T_{melt}–0.9 T_{cr}	3.47972	0.0285	0.41107	80.8884	0.08581	0.2	0.4
3B	T_{melt}–0.9 T_{cr}	3.86049	0.0292	0.50222	54.3992	0.05832	0.1	0.4
4C	T_{melt}–0.9 T_{cr}	3.96977	0.0295	0.53703	37.2634	0.04745	0.1	0.4
CO_2								
n.a.	T_{melt}–0.9 T_{cr}	3.50795	0.0272	0.76020	–	–	0.20	0.80
Methane								
n.a.	0.5 T_{cr}–0.9 T_{cr}	2.32038	0.0291	0.44718	–	–	0.35	1.97
Ethane								
n.a.	0.5 T_{cr}–0.9 T_{cr}	5.50926	0.0429	0.58463	–	–	0.29	1.38
Propane								
n.a.	0.5 T_{cr}–0.9 T_{cr}	9.15391	0.0587	0.66719	–	–	0.25	1.08
Iso-Butane								
n.a	0.5 T_{cr}–0.9 T_{cr}	12.92553	0.0751	0.71311	–	–	0.25	1.08

*n.a., non associating.

†%AAD $= \frac{1}{n}\sum_i \left|\frac{X_i^{cal} - X_i^{exp}}{X_i^{exp}}\right| \times 100$, where X stands for P^{sat} or ρ^{liq} and n is the number of experimental data points.

(see, e.g., Ref. 20). These interaction parameters have large values, they are strongly temperature dependent, and they cannot describe the phase behavior over extended temperature ranges including the LLE region.[21] EoS/G^E models have been also applied to H_2S-hydrocarbons. It was shown that, as for other size-asymmetric systems, classical EoS/G^E mixing rules like MHV2 and PSRK fail for very asymmetric mixtures, e.g., H_2S with alkanes heavier than pentadecane.[22–25] The deviations become progressively worse as the chain length of the hydrocarbon increases and, e.g., for H_2S-eicosane, MHV2 and PSRK yield errors around 30% or higher in pressure.[22] Other mixing rules like LCVM and the newest versions of PSRK[22–24,26] perform well for H_2S-alkanes. Still, none of these models has, to our knowledge, been applied to binary and especially multicomponent mixtures of H_2S with water, methanol, glycols, and hydrocarbons. For these polar mixtures, inevitably the performance of EoS/G^E models should be, in principle, determined by the activity coefficient models they are combined with.

The CPA Equation of State

The CPA EoS can be expressed for mixtures in terms of pressure P, as[27–29]:

$$P = \frac{RT}{V_m - b} - \frac{\alpha(T)}{V_m(V_m + b)} - \frac{1}{2}\frac{RT}{V_m}\left(1 + \rho\frac{\partial \ln g}{\partial \rho}\right)\sum_i x_i \sum_{A_i}(1 - X_{A_i}) \quad (1)$$

The key element of the association term is X_{A_i}, which represents the fraction of A-sites on molecule i that do not form bonds with other active sites, while x_i is the mole fraction of component i. X_{A_i} is related to the association strength $\Delta^{A_iB_j}$ between two sites belonging to two different molecules, e.g., site A on molecule i and site B on molecule j, determined from:

$$X_{A_i} = \frac{1}{1 + \rho\sum_j x_j \sum_{B_j} X_{B_j}\Delta^{A_iB_j}} \quad (2)$$

where the association strength $\Delta^{A_iB_j}$ in CPA is expressed as:

$$\Delta^{A_iB_j} = g(\rho)\left[\exp\left(\frac{\varepsilon^{A_iB_j}}{RT}\right) - 1\right] b_{ij}\beta^{A_iB_j} \quad (3)$$

with the radial distribution function $g(\rho) = \frac{1}{1 - 1.9\eta}$, the reduced density $\eta = \frac{1}{4}b\rho$ while $b_{ij} = \frac{b_i + b_j}{2}$. b_i is the temperature-independent covolume parameter of the component i and ρ is the molar density. The energy parameter of the EoS is given by a Soave-type temperature dependency:

$$\alpha(T) = a_o\left[1 + c_1(1 - \sqrt{T_r})\right]^2 \quad (4)$$

$T_r = \frac{T}{T_c}$ is the reduced temperature, while T_c is the experimental critical temperature. Finally, c_1 is a CPA parameter in the energy term (Eq. 4). In the expression for the association strength $\Delta^{A_iB_j}$, the parameters $\varepsilon^{A_iB_j}$ and $\beta^{A_iB_j}$ are called the association energy and the association volume, respectively. These two parameters are only used for associating components, and the three additional parameters of the SRK

Table 4. Pure Fluid Parameters (Obtained from Literature)

Fluid	Association Scheme*	a_0 (L^{2}bar mol^{-2})	b (L mol^{-1})	c_1	$\varepsilon^{A_iB_i}$ (bar L mol^{-1})	$\beta^{A_iB_j}$	References
n-Butane	n.a.	13.14274	0.07208	0.70771	–	–	13
Water	4C	1.22770	0.01451	0.67359	166.55	0.0692	13
Methanol	2B	4.05310	0.03098	0.43102	245.91	0.0161	13
Ethanol	2B	8.67160	0.04911	0.73690	215.32	0.0080	13
Ethylene glycol (MEG)	4C	10.819	0.0514	0.6744	197.52	0.0141	32
Diethylene glycol (DEG)	4C	26.408	0.0921	0.7991	196.84	0.0064	32
Triethylene glycol (TEG)	4C	39.126	0.1321	1.1692	143.37	0.0188	32

*n.a.: non associating.

Table 5. CPA Calculations for Water – H_2S Phase Equilibria (VLE and LLE)

					VLE		LLE	
					Water Rich Phase (Liquid)	H_2S Rich Phase (Vapor)	Water Rich Phase (Liquid)	H_2S Rich Phase (Liquid)
Temperature Range (K)	Association Sites in H_2S	k_{ij}	ε_{cross} (bar L mol^{-1})	β_{cross}	%AAD in x_{water}	% AAD in y_{water}	%AAD in x_{water}	% AAD in x_{water}
310.9–444.3	0	−0.0098	–	–	1.7	36	0.3	90
First approach								
	2d–0a	0.0985	mCR1: 83.275	0.0655	1.2	24	0.3	63
	1d–1a (2B)	0.2367	CR-1: 123.72	CR-1: 0.0771	1.3	>100	0.6	>100
	2d–1a (3B)	0.2601	CR-1: 110.47	CR-1: 0.0635	1.3	>100	0.6	>100
	2d–2a (4C)	0.2643	CR-1: 101.91	CR-1: 0.0573	1.5	>100	0.8	>100
Second approach								
	2d–0a	0.1913	Exp.: 108.78	0.0624	1.1	11	1.6	8
	1d–1a (2B)	0.1005	Exp.: 108.78	0.0590	1.2	17	0.4	17
	2d–1a (3B)	0.0991	Exp.: 108.78	0.0299	1.2	21	0.3	16
	2d–2a (4C)	0.0856	Exp.: 108.78	0.0188	1.2	23	0.4	21

Calculations using different association schemes for H_2S and the three approaches (zeroth, first, and second) described in "The CPA Equation of State" section (Experimental data from Refs. 36 and 37). *d*, proton donor; *a*, proton acceptor, $\%AAD = \frac{1}{n}\sum_i \left|\frac{X_i^{cal} - X_i^{exp}}{X_i^{exp}}\right| \times 100$, where X stands for mole fraction, x or y, and n is the number of experimental data points.

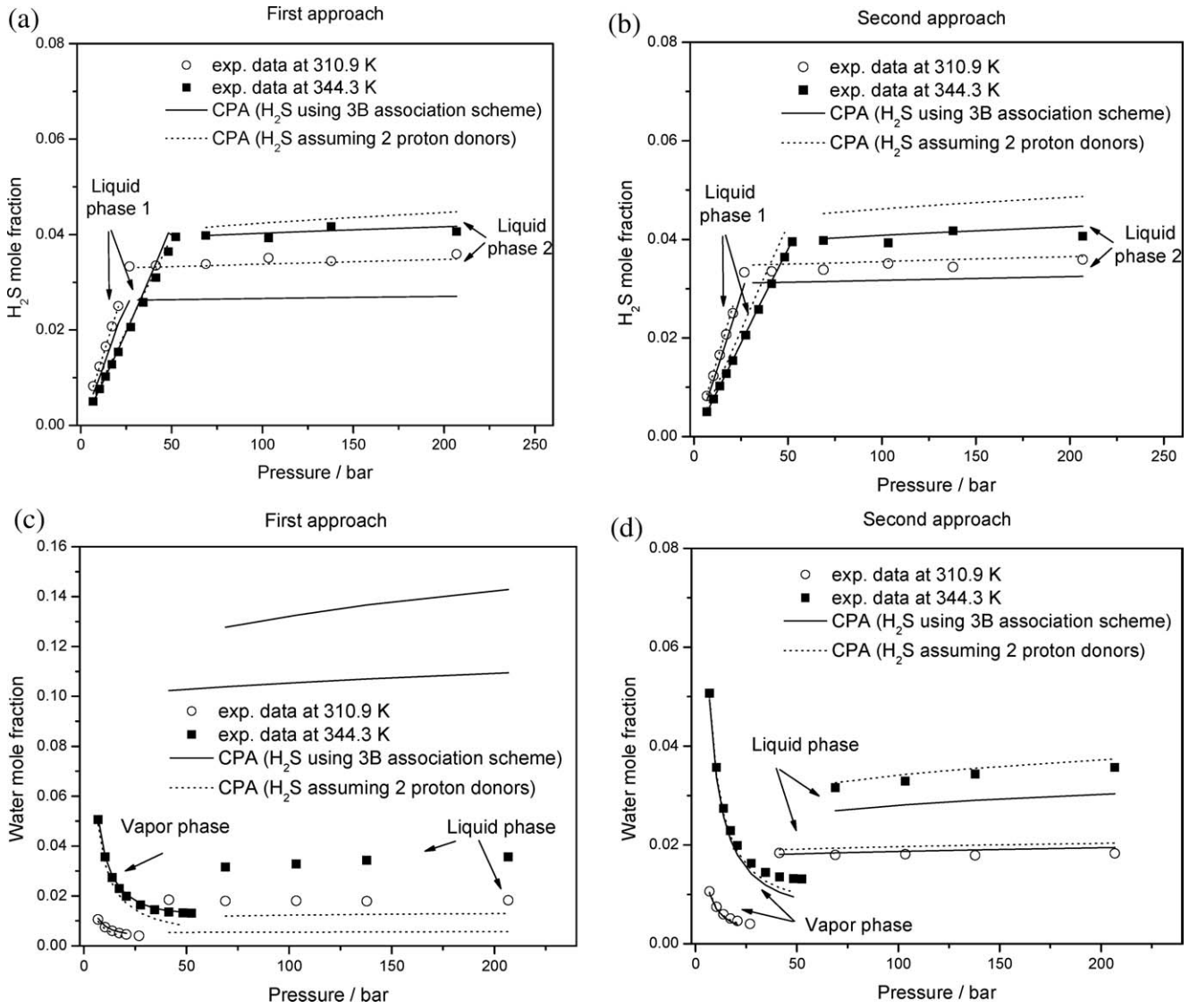

Figure 1. H_2S-water vapor-liquid and liquid-liquid equilibrium at 310.9 K and 344.3 K.

Smoothed data based on experimental measurements[36] and raw experimental data[37] (points) and CPA calculations (lines) using first and second approach. Water rich phase (a, b) and H_2S rich phase (c, d).

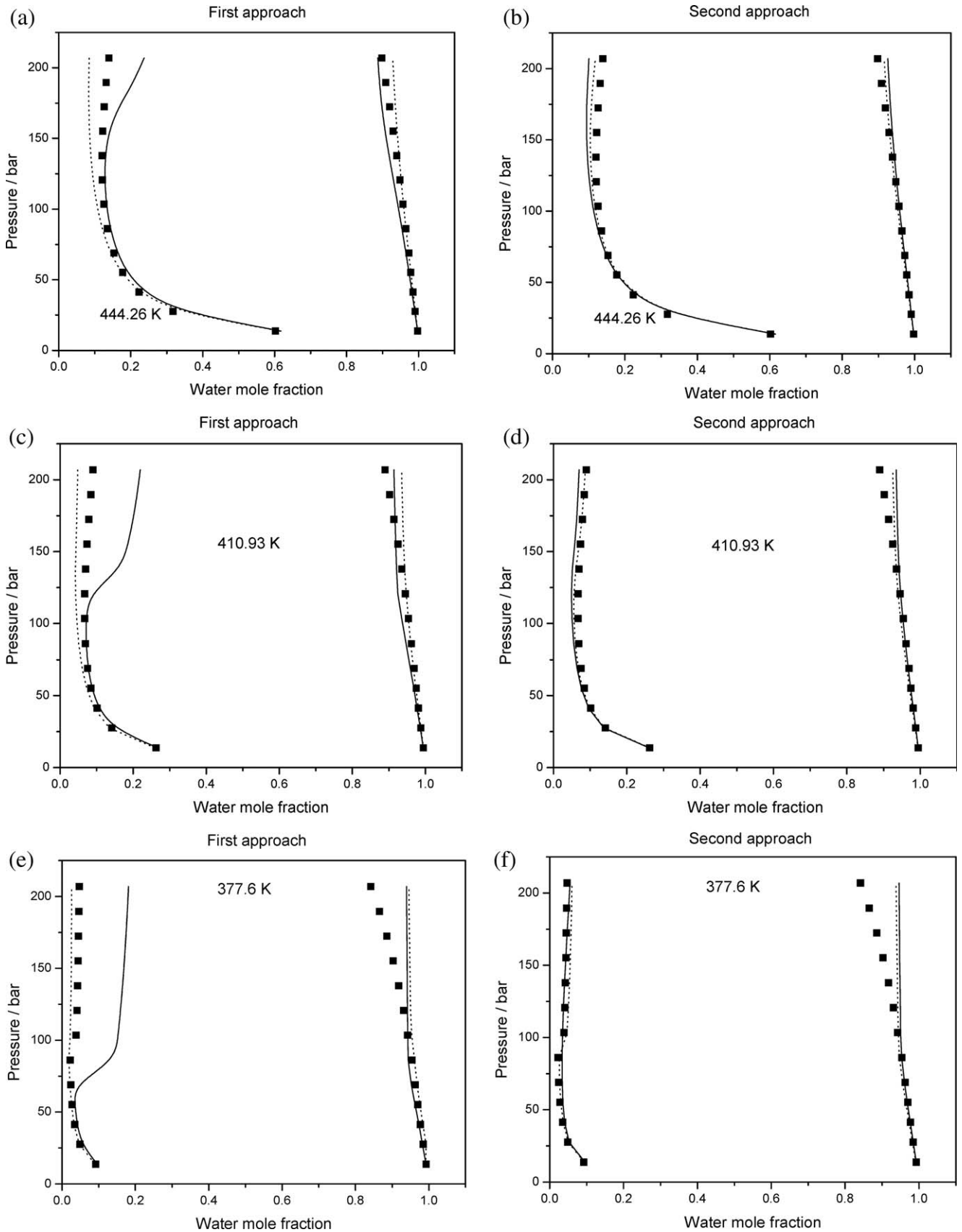

Figure 2. H_2S-water vapor-liquid equilibria.

Smoothed data[36] based on experimental measurements (points) and CPA calculations assuming that H_2S is self-associating fluid and using 3B associating scheme (solid lines) and that H_2S in non–self-associating fluid, but has two proton donors able to cross associate with water (dotted lines). Calculations using first and second approach.

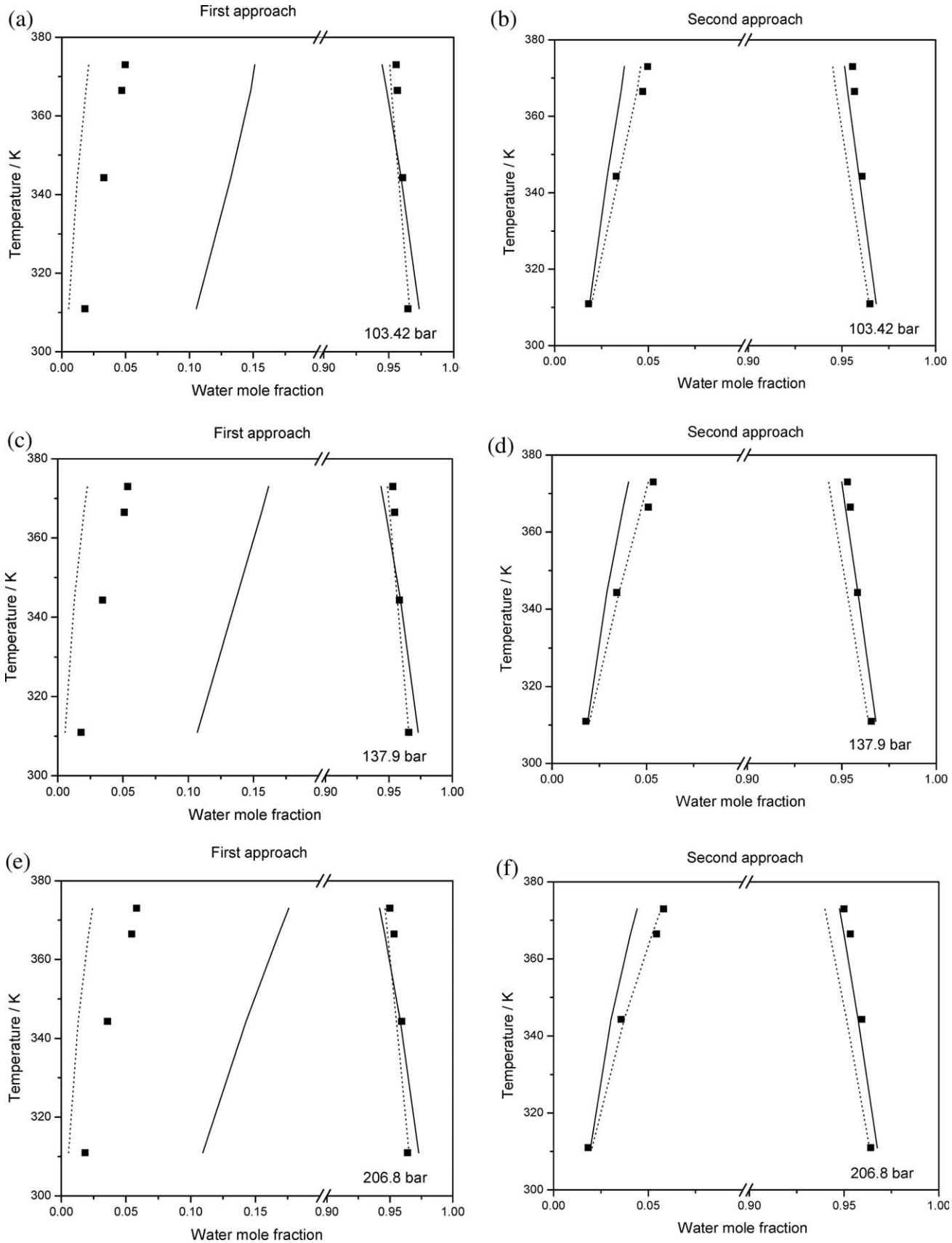

Figure 3. H_2S-water liquid-liquid equilibria.

Experimental data[37] (points) and CPA calculations assuming that H_2S is self-associating fluid and using 3B associating scheme (solid lines) and that H_2S in non–self-associating fluid, but has two proton donors able to cross associate with water (dotted lines). Calculations using first and second approach.

Table 6. CPA Calculations for H_2S (1) – Methanol (2) VLE

Temperature Range (K)	Pressure Range (bar)	Association Sites in H_2S	k_{ij}	ε_{cross} (bar L mol^{-1})	β_{cross}	%AAD in P	%AAD in y_1/y_2
298.1–398.1	0–92.9	0	−0.0353	–	–	8.7	2.8/24.4
First approach							
		2d–0a	0.0323	mCR1: 122.96	0.0333	5.9	3.3/22.0
		1d–1a (2B)	0.1368	CR-1: 163.40	CR-1: 0.0372	4.2	4.0/30.9
		2d–1a (3B)	0.1418	CR-1: 150.15	CR-1: 0.0306	3.7	3.9/29.5
		2d–2a (4C)	0.1465	CR-1: 141.59	CR-1: 0.0276	4.2	3.8/29.5
Second approach							
		2d–0a	0.0220	Exp.: 87.86	0.0988	5.5	3.5/22.5
		1d–1a (2B)	−0.1008	Exp.: 87.86	0.0900	3.2	3.5/24.3
		2d–1a (3B)	−0.0514	Exp.: 87.86	0.0658	3.3	3.6/24.0
		2d–2a (4C)	−0.0360	Exp.: 87.86	0.0516	3.1	3.6/24.0

Calculations using different association schemes for H_2S and the three approaches (zeroth, first, and second) described in "The CPA Equation of State" section (Experimental data[38]). d, proton donor; a, proton acceptor, $\%AAD = \frac{1}{n}\sum_i |(X_i^{cal} - X_i^{exp})/X_i^{exp}| \times 100$, where X stands for pressure, P, or mole fraction, y, and n is the number of experimental data points.

term (a_0, b, c_1) are the five pure compound parameters of the model. They are obtained by fitting vapor pressure and liquid density data. For inert components, e.g., hydrocarbons, only the three parameters of the SRK term are required, which can be obtained either from vapor pressures and liquid densities or calculated in the conventional manner (critical data, acentric factor). In this work, the former approach is adopted. In this study, H_2S was modeled as nonassociating as well as self-associating fluid using the 2B, 3B, and 4C association schemes (according to the terminology of Huang and Radosz[30]).

As before,[28,29] alcohols were modeled using the 2B association scheme, while water and glycols were modeled using the 4C association scheme.

In this work, parameters for all the examined pure fluids were estimated using saturated liquid density and vapor pressure data from DIPPR correlation[31] or when it was possible they were obtained from the literature. Pure fluid parameters are presented in Tables 3 and 4.

The performance of CPA in representing vapor pressures and liquid densities of H_2S is better than that of cubic equations of state, when compared to results presented in literature, even when H_2S is modeled as non–self-associating molecule. In the temperature region 193–323 K, Stamataki and Magoulas[2] report a deviation of 3–5% in vapor pressure and 0.7% in liquid volume of H_2S with various forms of translated PR EoS (the volume deviation is 6.5% with the original PR EoS). Much lower deviations are reported in Table 3; however, this is at the expense of a mismatch of the critical point.

When the CPA EoS is used for mixtures, the conventional mixing rules are employed in the physical term (SRK) for the energy and covolume parameters. The geometric mean rule is used for the energy parameter α_{ij}. The interaction

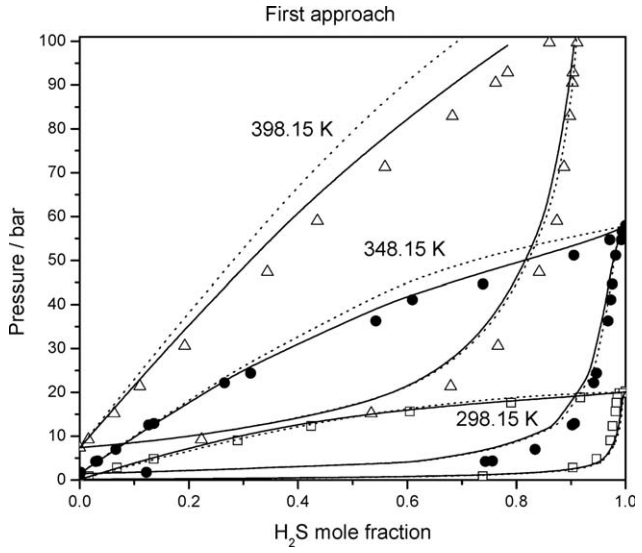

Figure 4. H_2S-Methanol vapor-liquid equilibria.

Experimental data[38] (points) and CPA calculations (lines) considering H_2S as inert compound (dotted lines) or that H_2S is non–self-associating fluid, but has one proton donor able to cross associate with water (solid lines).

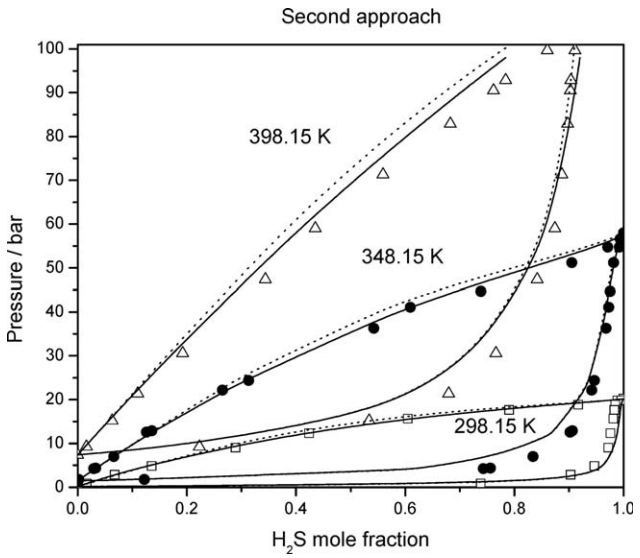

Figure 5. H_2S-methanol vapor-liquid equilibria.

Experimental data[38] (points) and CPA calculations assuming that H_2S is self-associating fluid and using 3B associating scheme (solid lines) and that H_2S is non–self-associating fluid, but has two proton donors able to cross associate with water (dotted lines).

Table 7. CPA Calculations for H_2S – Glycol VLE

	Temperature Range (K)	Association Sites in H_2S	k_{ij}	ε_{cross} (bar L mol^{-1})	β_{cross}	%AAD in P
MEG (1)-H_2S (2)	298.1–398.1	0	−0.0256	–	–	15.84
		1d–0a	0.0798	mCR1: 98.76	0.0970	11.40
		2d–0a	0.0779	mCR1: 98.76	0.0406	11.50
		1d–1a (2B)	0.1341	CR-1: 139.20	CR-1: 0.0348	15.13
		2d–1a (3B)	0.1498	CR-1: 125.96	CR-1: 0.0287	13.89
		2d–2a (4C)	0.1495	CR-1: 117.39	CR-1: 0.0259	15.69
DEG (1)-H_2S (2)		0	−0.0646		–	7.18
		1d–0a	−0.0598	mCR1: 98.42	0.0026	7.18
		2d–0a	−0.0590	mCR1: 98.42	0.0015	7.18
		1d–1a (2B)	0.0567	CR-1: 138.86	CR-1: 0.0234	13.18
		2d–1a (3B)	0.0739	CR-1: 125.62	CR-1: 0.0193	12.02
		2d–2a (4C)	0.0734	CR-1: 117.05	CR-1: 0.0174	13.40
TEG (1)-H_2S (2)		0	−0.0934		–	9.93
		1d–0a	−0.0933	mCR1: 71.68	0.0001	9.93
		2d–0a	−0.0932	mCR1: 71.68	0.0001	9.93
		1d–1a (2B)	0.0150	CR-1: 112.13	CR-1: 0.0402	12.85
		2d–1a (3B)	0.0321	CR-1: 98.88	CR-1: 0.0331	11.68
		2d–2a (4C)	0.0305	CR-1: 90.32	CR-1: 0.0299	12.77

Calculations using different association schemes for H_2S and two of the approaches (zeroth and first) are described in "The CPA Equation of State" section (Experimental data[39–41]). *d*, proton donor; *a*, proton acceptor, $\%AAD = \frac{1}{n}\sum_i^n \left|(P^{cal} - P^{exp})/P^{exp}\right| \times 100$, where P is the pressure and n is the number of experimental data points.

parameter k_{ij} is, for applications with aliphatic hydrocarbons and other inert (non–self-associating) molecules, the only adjustable binary parameter of CPA:

$$\alpha = \sum_i \sum_j x_i x_j \alpha_{ij}, \text{ where } \alpha_{ij} = \sqrt{\alpha_i \alpha_j}(1 - k_{ij}) \quad (5)$$

$$b = \sum_i x_i b_i \quad (6)$$

For extending the CPA EoS to mixtures of two associating compounds, e.g., alcohols or glycols with water, combining rules for the association energy ($\varepsilon^{A_iB_j}$) and the association volume ($\beta^{A_iB_j}$) are required. The CR-1 and the Elliott combining rule (ECR), described below, have been found successful in previous applications.

The expressions of the cross-association energy and cross-association volume parameters with CR-1 are:

$$\varepsilon^{A_iB_j} = \varepsilon_{cross} = \frac{\varepsilon^{A_iB_i} + \varepsilon^{A_jB_j}}{2} \text{ and } \beta^{A_iB_j} = \beta_{cross} = \sqrt{\beta^{A_iB_i}\beta^{A_jB_j}} \quad (7)$$

The expression of the cross-association strength ($\Delta^{A_iB_j}$) with ECR is:

$$\Delta^{A_iB_j} = \sqrt{\Delta^{A_iB_i}\Delta^{A_jB_j}} \quad (8)$$

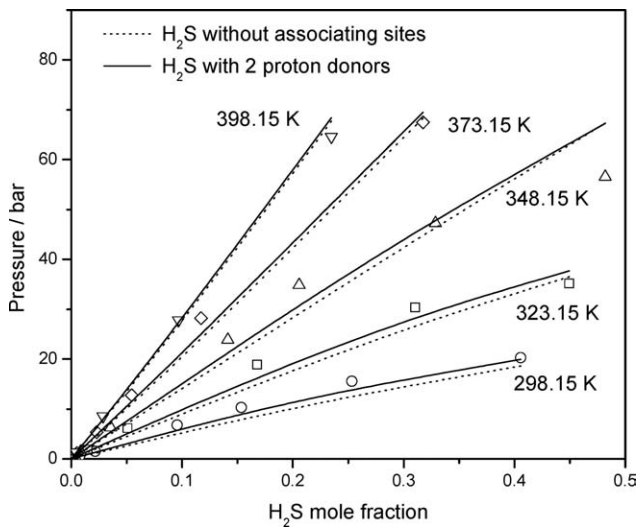

Figure 6. Solubility of H_2S in MEG.

Experimental data[39] (points) and CPA calculations (lines) considering H_2S as inert compound (dotted lines) or that H_2S has two (proton donors) association sites (solid lines).

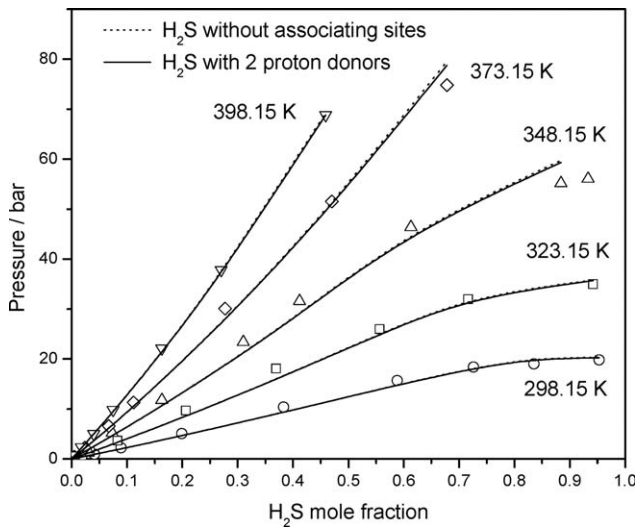

Figure 7. Solubility of H_2S in DEG.

Experimental data[40] (points) and CPA calculations (lines) considering H_2S as inert compound (dotted lines) or that H_2S has two (proton donors) association sites (solid lines).

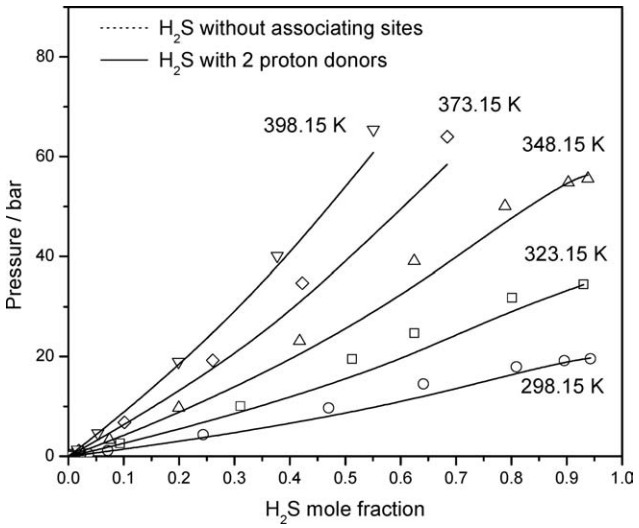

Figure 8. Solubility of H_2S in TEG.

Experimental data[41] (points) and CPA calculations (lines) considering H_2S as inert compound (dotted lines) or that H_2S has two (proton donors) association sites (solid lines).

To account for cross association (solvation), Folas et al. used the so-called modified CR-1 (mCR-1) rule[33]:

$$\varepsilon^{A_iB_j} = \frac{\varepsilon_{\text{associating}}}{2} \text{ and } \beta^{A_iB_j} = \beta_{\text{cross}} = \text{fitted} \qquad (9)$$

Then, the association strength will be estimated by Eq. 3 and in this way the in-built temperature dependency of the cross-association strength is retained for solvating systems. Previous calculations[34] have showed that this approach (using the modified CR-1 rule) yields satisfactory results, e.g., for water-aromatic hydrocarbons over large temperature ranges.

Three approaches, which are described below, are used in mixtures of H_2S with water or/and methanol. In mixtures of H_2S with all other fluids (hydrocarbons, glycols, or CO_2) only the zeroth and the first approach were used.

Zeroth approach

H_2S is considered as inert compound. No self-associating interactions between H_2S molecules are accounted for. Also, no cross association (solvation) is accounted for in mixtures of H_2S with other hydrogen bonding fluids, while the CR-1 rule (Eq. 7) is used for the water-methanol and water-MEG cross-association interactions. A single binary interaction parameter (k_{ij}) is optimized for each binary system by fitting the model to the experimental data.

First approach

In mixtures of two associating fluids, the CR-1 combining rule is used to estimate parameters for the cross-associating interactions (Eq. 7). A single binary interaction parameter (k_{ij}) is optimized for such binary systems.

In cases, in which solvation of H_2S (and CO_2) was assumed (i.e., when H_2S is modeled assuming that has only proton donor sites or when CO_2 is modeled assuming only proton acceptor sites), the modified CR-1 rule is used (Eq. 9). For all these binary systems, the cross-association volume (β_{cross}) and the binary interaction parameter (k_{ij}) are simultaneously optimized by fitting the model to the experimental data.

Second approach

In the second approach, effort has been made to incorporate in the model the strength of cross-associating interactions from experimental or theoretical studies of the literature, as discussed in "Previous Studies with Association (and other) Models for H2S Systems" section.

H_2S-H_2O mixtures exhibit a complicated phase behavior including the formation of solid, liquid and gas phases. To model this system, the formation of weak hydrogen bonds between water and H_2S molecules is assumed. The hydrogen bonding energy for the cross association is set equal to the experimental value (–10,878 J mol^{-1}).[7] In the same direction, the formation of weak hydrogen bonds is assumed between alcohol and H_2S molecules. The hydrogen bonding energy for the cross association is set equal to the experimental value of the H_2S-ethanol interaction (–8786 J mol^{-1}).[11] Moreover, for one of the multicomponent systems considered, the CO_2-water system is present and for this the experimental cross-association energy value equal to –14,200 J mol^{-1} is used.[35] For all these binary systems, the cross-association volume (β_{cross}) and the binary interaction parameter (k_{ij}) are simultaneously optimized by fitting the model to the experimental data.

Binary Mixtures

H_2S-water

Firstly, the vapor-liquid and liquid-liquid equilibria of water-H_2S system was modeled using the three approaches described in "The CPA Equation of State" section. Unlike all other binary H_2S-systems considered in this work, there is an area of immiscibility in the H_2S-water mixture. Phase split occurs between an aqueous phase with 3–4% dissolved H_2S and a H_2S-rich liquid phase with approximately 3% water.[4] It is thus interesting to see that the polar nature of H_2S alone is not sufficient to render the molecule fully

Table 8. CPA Calculations for H_2S-CO_2 VLE Using Different Association Schemes for H_2S (Experimental data[42])

	Temperature Range (K)	Association Sites in H_2S	Association Sites in CO_2	k_{ij}	ΔT	Δy
H_2S-CO_2	254.1–349.3	0	0	0.1179	1.09	0.0092
		1d–1a (2B)	0	0.0356	1.32	0.0149
		2d–1a (3B)	0	0.0519	1.15	0.0118
		2d–2a (4C)	0	0.0543	1.10	0.0102

d, proton donor; *a*, proton acceptor; $\Delta X = \frac{1}{n}\sum_i \left|X^{\text{exp}} - X^{\text{calc}}\right|$, where X stands for temperature, T, or mole fraction, y, and n is the number of experimental data points.

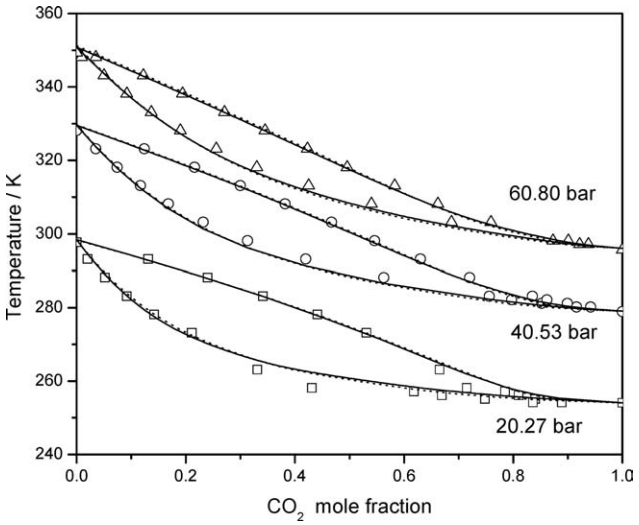

Figure 9. CO_2-H_2S VLE.

Experimental data[42] (points) and CPA calculations (lines) considering H_2S and CO_2 as inert compounds (solid lines) or that H_2S has three (3B) association sites (dotted lines).

miscible with water at all conditions. The results are presented in Table 5, while some characteristic calculations are presented in Figures 1–3.

Using both the first and second approach, the lowest deviations from experimental data are observed if H_2S is modeled as non–self-associating fluid, but assuming that it has two proton donor sites (2d–0a) that are able to cross associate with water's proton acceptor sites (solvation). Relatively higher deviations from experimental data are observed if H_2S is modeled as nonassociating fluid. Very high deviations from experimental data are observed when H_2S is modeled as self-associating fluid (2B, 3B, 4C) and the CR-1 rule is used (thus only fitting one interaction parameter, the k_{ij}). If, however, the experimental cross-association energy is used, then the correlation is satisfactory (fitting in this case two interaction parameters, k_{ij} and β_{cross}). In this context, the results with the 3B scheme for H_2S are particularly promising, even for high pressure LLE, as can be seen in Figure 3.

H_2S-methanol

Next, the vapor-liquid equilibria of methanol-H_2S system was modeled using the three approaches described in "The CPA Equation of State" section. Results are presented in Table 6, while characteristic calculations are presented in Figures 4 and 5.

Relatively high deviations from experimental data are observed if H_2S is modeled as inert compound. Using the first approach, the lowest deviations from experimental data are observed if H_2S is modeled assuming that it has only proton donor sites (2d–0a) that are able to cross associate with alcohol molecules. In the second approach (experimental cross-association energy), all the examined association schemes result in similar deviations from experimental data.

H_2S-glycols

For H_2S-glycol mixtures, calculations were performed using the zeroth and the first approach described in "The CPA Equation of State" section. The second approach was not used as there are not, to our knowledge, experimental data for the cross-association energy between H_2S and glycols. The results are presented in Table 7 and Figures 6–8.

Calculations for mixtures of H_2S with glycols are in very satisfactory agreement with experimental data even when

Table 9. CPA Calculations for H_2S – Hydrocarbon Mixtures

System	Temperature Range (K)	Pressure Range (bar)	Association Sites in H_2S	%AAD in P	%AAD in y_1	k_{ij}	%AAD in P	%AAD in y_1
				$k_{ij}=0$				
Methane (1)-H_2S (2)	277.6–344.3	11.6–120	0	14.5	11.7	0.0760	3.0	5.7
			1d–1a (2B)	6.1	6.5	0.0338	3.2	4.9
			2d–1a (3B)	4.9	5.6	0.0221	3.7	5.6
			2d–2a (4C)	4.0	5.0	0.0148	3.6	5.5
Ethane (1)-H_2S (2)	227.9–283.1	2.0–30.2	0	12.6	13.4	0.0847	1.7	1.7
			1d–1a (2B)	3.4	5.7	0.0356	3.0	2.2
			2d–1a (3B)	4.8	5.9	0.0373	1.2	1.4
			2d–2a (4C)	4.9	5.6	0.0329	0.7	1.4
Butane (1)-H_2S (2)	366.4–418.1	13.5–71	0	4.2	7.3	0.0897	1.6	2.5
			1d–1a (2B)	1.3	3.5	−0.0114	1.3	3.8
			2d–1a (3B)	2.1	3.7	0.0249	1.4	2.8
			2d–2a (4C)	2.3	3.8	0.0328	1.5	2.7
Iso-butane(1)-H_2S(2)	344.2–383.2	11.1–60.9	0	4.4	8.9	0.0761	1.9	1.7
			1d–1a (2B)	1.9	2.0	−0.0239	1.4	2.9
			2d–1a (3B)	1.6	2.7	0.0084	1.7	2.1
			2d–2a (4C)	1.8	2.9	0.0166	1.8	1.8
				ΔT	%AAD in y_1		ΔT	%AAD in y_1
Propane (1)-H_2S (2)	216.9–344.2	1.4–27.6	0	5.3	21.1	0.0917	0.71	17.5
			1d–1a (2B)	1.08	9.1	0.0050	1.10	8.8
			2d–1a (3B)	1.62	8.0	0.0306	0.66	11.4
			2d–2a (4C)	1.88	8.6	0.0325	0.53	13.2

Calculations using different association schemes for H_2S and the zeroth approach (i.e. no solvation is included and only one interaction parameter is used) described in "The CPA Equation of State" section (experimental data[43–46]). *d*, proton donor; *a*, proton acceptor, $\%AAD = \frac{1}{n}\sum_i \left|\frac{X_i^{cal}-X_i^{exp}}{X_i^{exp}}\right| \times 100$, where X stands for pressure, P, or mole fraction, y, and n is the number of experimental data points, $\Delta T = \frac{1}{n}\sum_i \left|T^{exp} - T^{calc}\right|$, where T is the temperature and n is the number of experimental data points.

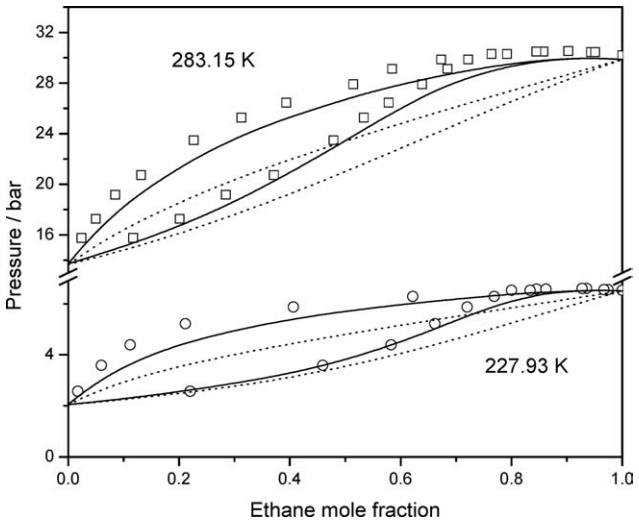

Figure 10. H_2S-ethane VLE.

Experimental data[44] (points) and CPA predictions ($k_{ij} = 0$) considering H_2S as inert compound (dotted line) and assuming that H_2S is self-associating fluid and using the 3B associating scheme (solid line).

H_2S is treated as inert compound. Assuming solvation of H_2S in glycols (i.e., assuming that H_2S has only proton donor sites that are able to cross associate with glycols) improves calculations only for H_2S-MEG mixture. The results are in agreement to previous recent investigations published with CPA in the literature.[13,14] Compared to the solvation case, slightly worse results are obtained when H_2S is considered to be a self-associating fluid. Important to recall, however, that in the latter case only the k_{ij} is optimized while when solvation is assumed with modified CR-1 rule two interaction parameters are fitted to experimental data.

H_2S-CO_2

For H_2S-CO_2 mixtures, calculations were performed considering H_2S as inert compound or that H_2S is self-associating fluid and using 2B, 3B, and 4C associating schemes. In all cases, CO_2 was modeled as inert compound and, subsequently, no cross association was assumed. Results are presented in Table 8 and Figure 9. Very satisfactory results were obtained in all cases.

H_2S-hydrocarbons

The vapor-liquid equilibrium of H_2S-hydrocarbon mixtures was modeled using different association schemes for H_2S.

Table 10. Binary Interaction Parameters used in Modeling H_2S-CO_2-CH_4

	Methane	H_2S
Methane	–	$k_{ij} = 0.0760$
CO_2	$k_{ij} = 0.0882$	$k_{ij} = 0.1179$

The results are presented in Table 9 for model predictions (using no binary interaction parameter, $k_{ij} = 0$) and model correlations using a binary interaction parameter optimized based on the experimental data ($k_{ij} \neq 0$). Using no binary interaction parameter ($k_{ij} = 0$), the higher deviations from experimental data are observed if H_2S is modeled as inert compound. In this case, the model fails to predict the appearance of the azeotrope in mixtures of H_2S with ethane or propane. The appearance of the azeotrope is predicted in all other cases (i.e., if H_2S is modeled as self-associating fluid). These two systems (H_2S-ethane and H_2S-propane) are the only H_2S-paraffin mixtures, which are known to exhibit azeotropy.[1,18] One typical result—CPA predictions—is presented in Figure 10 for the vapor-liquid equilibrium of H_2S-ethane system. The results are in agreement with Ruffine et al.[12] who performed similar calculations. On the other hand, if a nonzero binary interaction parameter is used the CPA model accurately describes the phase behavior of all examined systems, including the appearance of the azeotrope.

As mentioned in "Previous Studies with Association (and other) Models for H_2S Systems" section. H_2S-alkane systems have been extensively studied with various variants of the PR EoS by Stamataki and Magoulas[2] and Carroll and Mather[1,18] (for alkanes up to eicosane). The binary interaction parameter, k_{ij}, decreases with chain length and reaches negative values for mixtures of H_2S with alkanes above pentadecane or hexadecane. The k_{ij} values presented for the H_2S mixtures with the alkanes considered here are similar to those shown in Table 9 (0.093/0.083 for methane, 0.082/0.089 for ethane, 0.087/0.089 for propane, and 0.085/0.06 for butane).

Multicomponent Mixtures

The H_2S-CO_2-CH_4 mixture

The H_2S-CO_2-methane system was modeled considering that acid gases do not have any association site. The binary interaction parameters were adopted from the corresponding binary mixtures and are presented in Table 10, while the results are shown in Table 11 and in Figure 11. In all cases, CPA model predictions are in very satisfactory agreement with the experimental data, even when the acid gases are modeled without any association sites.

Table 11. $\%\Delta x$ and $\%\Delta y$ for H_2S (1)-CH_4 (2)-CO_2 (3) VLE (Experimental Data from Ref. 47)

Temperature (K)	Pressure(bar)	Association Sites CO_2-H_2S	$\%\Delta x_1$	$\%\Delta x_2$	$\%\Delta x_3$	$\%\Delta y_1$	$\%\Delta y_2$	$\%\Delta y_3$
222.15	20.68	0–0	1.17	0.86	1.25	1.03	1.08	1.42
	34.47	0–0	1.04	1.81	1.18	1.43	2.41	1.44
	48.26	0–0	1.06	3.51	2.77	1.15	1.52	1.85
238.75	20.68	0–0	1.19	0.95	1.00	1.60	1.13	0.78
	34.47	0–0	0.92	0.43	0.73	1.43	1.91	1.31
	48.26	0–0	1.54	1.51	1.56	0.91	2.04	1.57

$\%\Delta x = \frac{1}{n}\sum_i \left|X_i^{\text{cal}} - X_i^{\text{exp}}\right| \times 100$, where X is the mole fraction, x or y, and n is the number of experimental data points.

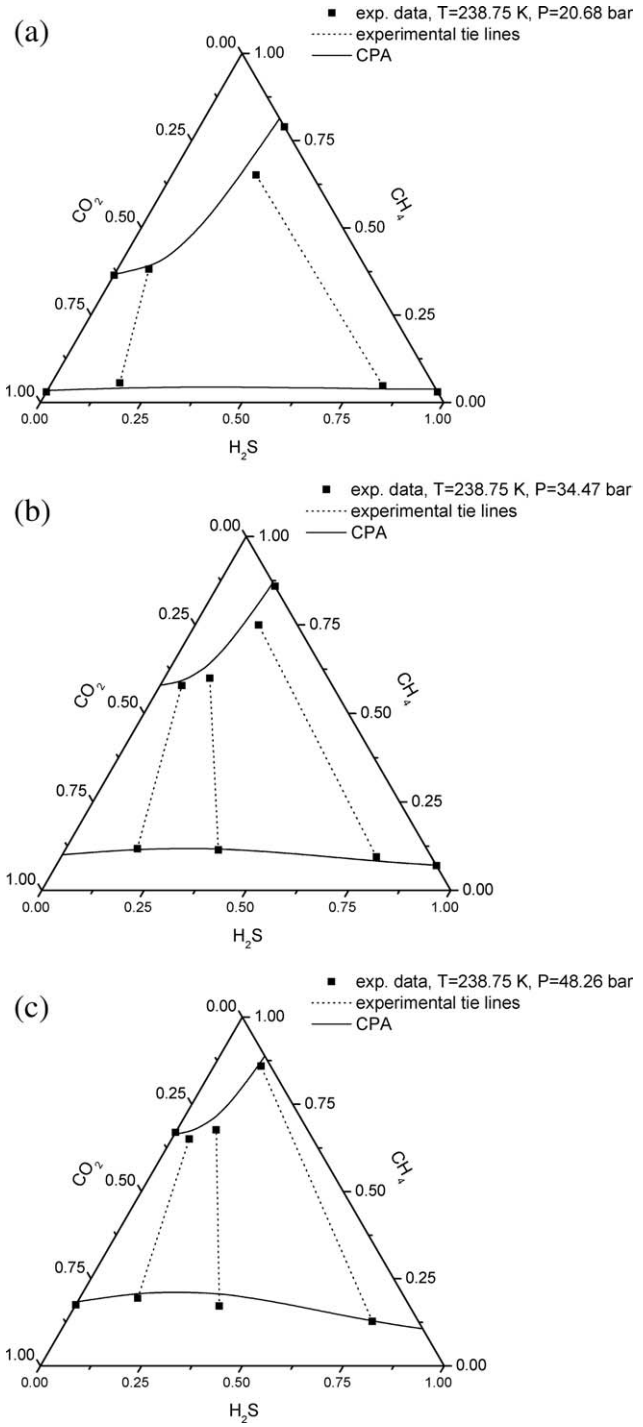

Figure 11. H_2S-CH_4-CO_2 VLE at 238.75 K and 20.68 bar (a), 34.47 bar (b), 48.26 bar (c).

Quaternary mixtures

Three quaternary mixtures were modeled using different association schemes. In all cases, binary interaction and solvation parameters were adopted from the corresponding binary systems.

The CR-1 rule is always used for the cross-associating mixtures water-methanol and water-MEG, while either the modified CR-1 rule or the experimental value for the cross-association energies are used for mixtures of acid gases with water and methanol. Because of the lack of experimental values, the modified CR-1 rule is always used for H_2S-MEG.

Table 12. Binary Parameters for Case A

	k_{ij}	ε_{cross} (bar L mol^{-1})	β_{cross}
H_2O-methanol	−0.0748	CR-1: 206.23	CR-1: 0.0334
H_2O-MEG	−0.0199	CR-1: 182.04	CR-1: 0.0312
H_2O-H_2S	−0.0098	–	–
H_2S-methanol	−0.0353	–	–
CH_4-H_2O	0.0098	–	–
CH_4-Methanol	0.0528	–	–
CH_4-H_2S	0.0760	–	–
H_2O-CO_2	−0.0232	–	–
H_2S-CO_2	0.1179	–	–
CH_4-CO_2	0.0882	–	–
H_2S-MEG	−0.0253	–	–
CH_4-MEG	0.1754	–	–

More specifically, the following modeling approaches were considered for multicomponent H_2S-containing systems:

Case A. H_2S (and CO_2) are modeled as inert compounds: No H_2S (and CO_2) self-associating interactions are assumed. Also, no cross-associating interactions are assumed between acid gases (H_2S, CO_2) and methanol, water, or MEG.

Case B1. Solvation of H_2S and CO_2: Acid gases are modeled as non–self-associating fluids, however cross-association interactions with water, methanol, and MEG were assumed. H_2S is modeled assuming that it has two proton donors, which are only able to cross associate with water, methanol, or MEG. CO_2 is modeled assuming that it has two proton acceptor sites, which are only able to cross associate with water. The mCR-1 combining rule is used to obtain parameters for the aforementioned cross interactions (first approach in "The CPA Equation of State" section).

Case B2. Solvation of H_2S and CO_2: Acid gases are modeled as non–self-associating fluids, however cross-association interactions with water, methanol, and MEG were assumed. H_2S is modeled assuming that it has two proton donors, which are only able to cross associate with water, methanol, or MEG. CO_2 is modeled assuming that it has one proton acceptor site, which is only able to cross associate with water. The association energy for the cross interactions between H_2S-water, H_2S-–methanol, and between CO_2-water is adopted from experimental studies (second approach described in "The CPA Equation of State" section). The

Table 13. Binary Parameters for Case B1

	k_{ij}	ε_{cross} (bar L mol^{-1})	β_{cross}
H_2O-methanol	−0.0748	CR-1: 206.23	CR-1: 0.0334
H_2O-H_2S	0.0985	mCR1: 83.275	0.0654
H_2S-methanol	0.0323	mCR1: 122.96	0.0333
H_2O-CO_2	0.1380	mCR1: 83.275	0.0911
H_2O-MEG	−0.0199	CR-1: 182.04	CR-1: 0.0312
H_2S-MEG	0.0779	mCR1: 98.76	0.0406
CH_4-H_2O	0.0098	–	–
CH_4-methanol	0.0528	–	–
CH_4-H_2S	0.0760	–	–
H_2S-CO_2	0.1179	–	–
CH_4-CO_2	0.0882	–	–
CH_4-MEG	0.1754	–	–

Table 14. Binary Parameters for Case B2

	k_{ij}	ε_{cross} (bar L mol^{-1})	β_{cross}
H_2O-methanol	−0.0748	CR-1: 206.23	CR-1: 0.0334
H_2O-H_2S	0.1913	Exp.: 108.78	0.0624
H_2S-methanol	0.0220	Exp.: 87.86	0.0988
H_2O-MEG	−0.0199	CR-1: 182.04	CR-1: 0.0312
H_2S-MEG	0.0779	mCR1: 98.76	0.0406
H_2O-CO_2	0.1141	Exp: 142.00	0.0162
CH_4-H_2O	0.0098	–	–
CH_4-methanol	0.0528	–	–
CH_4-H_2S	0.0760	–	–
CH_4-MEG	0.1754	–	–
H_2S-CO_2	0.1179	–	–
CH_4-CO_2	0.0882	–	–

Table 16. Binary Parameters for Case C2

	k_{ij}	ε_{cross} (bar L mol^{-1})	β_{cross}
H_2O-ethanol	−0.0748	CR-1: 206.23	CR-1: 0.0334
H_2O-H_2S	0.0991	Exp.: 108.78	0.0299
H_2S-ethanol	−0.0514	Exp.: 87.86	0.0658
H_2O-CO_2	0.1141	Exp: 142.00	0.0162
H_2O-MEG	−0.0199	CR-1: 182.04	CR-1: 0.0312
H_2S-MEG	0.1498	CR-1: 125.96	CR-1: 0.0287
CH_4-H_2O	0.0098	–	–
CH_4-methanol	0.0528	–	–
CH_4-H_2S	0.0221	–	–
H_2S-CO_2	0.0519	–	–
CH_4-CO_2	0.0882	–	–
CH_4-MEG	0.1754	–	–

mCR-1combining rule is used to obtain parameters for the H_2S-MEG association (no experimental values available).

Case C1: H_2S Was Modeled as Self-Associating Fluid Using the 3B Association Scheme. CO_2 was modeled assuming that it has two proton acceptor sites that are only able to cross associate with water. The CR-1 combining rule is used to obtain parameters for cross interactions.

Case C2: H_2S Was Modeled as Self-Associating Fluid Using the 3B Association Scheme. CO_2 was modeled assuming that it has one proton acceptor site, which is only able to cross associate with water. The association energy for the cross interactions between H_2S-water, CO_2-water, and H_2S-methanol is adopted from experimental studies (second approach described in "The CPA Equation of State" section).The CR-1 combining rule was used to obtain parameters for the H_2S-MEG association (no experimental values available).

The interaction parameters for the binary systems involved in the modeling of the three multicomponent mixtures (H_2O-methanol-H_2S-CH_4, H_2O-CO_2-H_2S-CH_4, and H_2O-MEG-H_2S-CH_4) are presented for all cases in Tables 12–16. The results are summarized in terms of deviations between experimental and predicted compositions in the vapor and liquid phases in Tables 17–19.

Discussion of the Results for the Multicomponent Systems

To facilitate the discussion we call the three H_2S containing quaternary mixtures as the "methanol," the "CO_2," and the "MEG" systems, for which respectively the results were presented in Tables 17–19. The last row of these three tables indicates which methodology provides the lowest deviations. Often more than one approach is indicated if results (percentage deviations) are quite similar.

Table 15. Binary Parameters for Case C1

	k_{ij}	ε_{cross} (bar L mol^{-1})	β_{cross}
H_2O-methanol	−0.0748	CR-1: 206.23	CR-1: 0.0334
H_2O-H_2S	0.2601	CR-1: 110.47	CR-1: 0.0635
H_2S-methanol	0.1418	CR-1: 150.15	CR-1: 0.0306
H_2O-CO_2	0.1380	mCR1: 83.275	0.0911
H_2O-MEG	−0.0199	CR-1: 182.04	CR-1: 0.0312
H_2S-MEG	0.1498	CR-1: 125.96	CR-1: 0.0287
CH_4-H_2O	0.0098	–	–
CH_4-methanol	0.0528	–	–
CH_4-H_2S	0.0221	–	–
H_2S-CO_2	0.0519	–	–
CH_4-CO_2	0.0882	–	–
CH_4-MEG	0.1754	–	–

The overall predictive performance of CPA is satisfactory. For all three systems, rather higher errors are observed for the small concentrations of methane in the liquid phase. For the "methanol" and "MEG" systems, relatively high deviations are obtained for the concentration of water in the vapor phase, and also for the rather low MEG concentration in the vapor phase.

As can be seen from the last row of Tables 17–19, different approaches may perform better in predicting concentrations of the various components in the vapor and liquid phases. Still, some conclusions can be drawn. The approaches C2 and B2 appear to be the best for the CO_2 and the MEG systems, while C1 and B1 are the best for the methanol system. Thus, the best results are indeed obtained if solvation is explicitly accounted for (B1, B2), especially when the cross-association energy is obtained from the experimental data (B2). Very good results are also obtained if H_2S is assumed to be a self-associating molecule (3B scheme), especially again when the cross-association energy is taken from independent measurements (C2) rather than from the modified CR-1 rule.

To understand the somewhat different best choices for the "methanol" system, Table 20 summarizes the experimental (from spectroscopic and calorimetric measurements) and calculated cross-association energies (and volumes) for mixtures of H_2S or CO_2 with water and alcohols. The calculated values are estimated using the modified CR-1 rule.

As mentioned, approaches B2 and C2 employ the experimental values, while approaches B1 and C1 employ the modified CR-1 rule. In both cases, for solvating binary mixtures, two interaction parameters are fitted to experimental data, so the difference in the multicomponent predictions deserves some analysis. As can be seen in Table 20, the adopted "experimental" cross-association energy for H_2S-methanol is smaller than the value for H_2S-water, while the modified CR-1 rule predicts the opposite. However, due to lack of available experimental data for H_2S-methanol interactions, the former value was adopted from H_2S-ethanol.[11]

Table 21 provides the Kamlet-Taft solvatochromic parameters of several compounds discussed in this work. These parameters can be used for quantifying the Lewis acid (LA)-Lewis base (LB) interactions. It can be seen that methanol and ethanol have both an acidic and basic character, but

Table 17. Summarized Deviations from Experimental Data for H_2O (1)-Methanol (2)-H_2S (3)-CH_4 (4) VLE (Experimental Data from Ref. 48)

	x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_4
Case A: H_2S inert								
%AAD	0.6	0.7	29	63	50	15	13	1.1
Case B1: Solvation of H_2S (mCR-1)								
%AAD	0.5	0.7	23	64	47	8.0	10	0.8
Case C1: H_2S self associating 3B (CR-1)								
%AAD	0.5	0.8	16	68	34	25	7.1	0.6
Case B2: Solvation of H_2S (experimental values for ε_{cross})								
%AAD	0.8	0.9	39	68	42	11	17	1.3
Case C2: H_2S self associating 3B (experimental values for ε_{cross})								
%AAD	0.6	0.8	27	65	44	10	11	1.0
Lowest deviation	C1, B1	B1 (All except for B2)	C1	B1	C1	B1	C1, B1	C1, B1

$\%AAD = \frac{1}{n}\sum_i \left|\frac{X_i^{cal} - X_i^{exp}}{X_i^{exp}}\right| \times 100$, where X stands for mole fractions, x or y, and n is the number of experimental data points.

these are not identical. We should thus be expecting somewhat different solvation characteristics with other molecules.

Consequently, unlike in the cases of CO_2 and MEG systems, for the methanol multicomponent system, there is the important assumption when using the experimental cross-association values, that the value between H_2S-methanol is taken from H_2S-ethanol. A slightly higher value than the one used (which could be anticipated) will be closer to the mCR-1 value and the results will be improved.

Comparison to Previous Investigations

Very few investigations with other models have been presented in the literature for the multicomponent systems discussed here. We have not found any other models tested for the two systems containing methanol and glycol, while the CO_2-H_2S-water-methane quaternary was studied by Knudsen et al.[51] with cubic EoS and various mixing rules, Vafaie-Sefti et al.[52] with an association equation of state and recently by Li and Firoozabadi[17] with their PR-CPA, discussed in "Previous Studies with Association (and other) Models for H_2S Systems" section.

Knudsen et al.[51] used the SRK EoS with various mixing rules. For multicomponent mixtures, they concluded that going from three temperature independent binary parameters to six binary parameters (temperature dependent parameters) does not necessarily improve the phase equilibrium results. Deviations from experimental data using three or more binary parameters are comparable with the deviations of this study using one or two temperature independent binary parameters.

Vafaie-Sefti et al.[52] used a new association EoS and they obtained relatively small deviations from experimental data even without using any binary interaction parameter ($k_{ij} = 0$).

Li and Firozabadi[17] used two temperature dependent parameters for water-CO_2 and water-H_2S binary systems, as well as one parameter for the remaining nonassociating binary mixtures. Similarly to our observations, they report that the predictions of the water mole fraction in the H_2S rich phase are significantly improved when cross-association interactions between water and H_2S or CO_2 are accounted for.

Conclusions

The CPA equation of state is applied to binary and multicomponent systems containing H_2S with other compounds, both nonpolar (alkanes, CO_2) and polar ones (water, methanol, and MEG). Judging from its physical properties and according to various theoretical literature studies, only very weak hydrogen bonding interactions may occur between H_2S molecules. If, however, this weak self-association is accounted for using three association sites, then CPA can predict the appearance of the azeotrope in H_2S-small hydrocarbon mixtures. Without accounting for self-association of H_2S, the azeotrope can be correlated using an interaction parameter.

Table 18. Deviations from Experimental Data for the H_2O (1)-CO_2 (2)-H_2S (3)-CH_4 (4) Quaternary Mixture (Experimental Data from Ref. 49, Mixture with Overall Composition H_2O 0.5, CO_2 0.3, H_2S 0.05, CH_4 0.15 mol)

	x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_4
Case A: CO_2 and H_2S inerts								
%AAD	0.4	27	9.4	69	30	0.63	2.9	1.6
Case B1: Solvation of CO_2 and H_2S (2 proton acceptors in CO_2 and 2 proton donors in H_2S) (mCR-1)								
%AAD	0.5	39	13	75	8.9	1.0	2.7	1.3
Case C1: H_2S 3B, solvation of CO_2 in water (CR-1 and mCR-1, respectively)								
%AAD	0.5	40	21	78	20	1.0	2.3	1.1
Case B2: Solvation of CO_2 and H_2S (experimental values for ε_{cross})								
%AAD	0.2	11	16	71	14	0.7	2.9	1.2
Case C2: H_2S 3B, solvation of CO_2 in water (experimental values for ε_{cross})								
%AAD	0.2	10	8.3	70	11	0.7	2.5	1.2
Lowest deviation	C2, B2	C2, B2	C2, B1	A, C2 (all)	B1, C2	A, C1, C2	C1, C2	C1, C2

$\%AAD = \frac{1}{n}\sum_i \left|\frac{X_i^{cal} - X_i^{exp}}{X_i^{exp}}\right| \times 100$, where X stands for mole fractions, x or y, and n is the number of experimental data points.

Table 19. Deviations from Experimental Data for the H_2O (1)-MEG (2)-H_2S (3)-CH_4 (4) Quaternary Mixture (Experimental Data from Ref. 48)

	x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_4
Case A: H_2S inert								
%AAD	1.3	1.3	92	77	58	89	19	1.7
Case B1: Solvation of H_2S (mCR-1)								
%AAD	0.9	0.8	55	76	52	85	11	1.0
Case C1: H_2S 3B (CR-1)								
%AAD	0.8	0.7	45	80	36	70	9.0	0.8
Case B2. Solvation of H_2S (experimental values for ε_{cross})								
%AAD	0.2	0.2	4.2	71	50	89	1.4	0.1
Case C2: H_2S self associating 3B (experimental values for ε_{cross})								
%AAD	0.6	0.5	33	76	45	70	6.4	0.6
Lowest deviation	B2	B2	B2	B2 (all)	C1, C2	C2, C1	B2, C1	B2

$\%AAD = \frac{1}{n}\sum_i \left|\frac{X_i^{cal} - X_i^{exp}}{X_i^{exp}}\right| \times 100$, where X stands for mole fractions, x or y, and n is the number of experimental data points.

Table 20. Association Parameters Using Two Different Approaches

	Experimental Values (Approach 2)		Modified CR-1 (Approach 1)	
System	ε_{cross} (L bar mol^{-1})	β_{cross} (Optimized by the exp. data)	ε_{cross} (L bar mol^{-1})	β_{cross} (Optimized by the Exp. Data
H_2S-water	108.78	0.0624	166.55/2 = 83.27	0.0655
H_2S-methanol	87.86*	0.0988	245.91/2 = 122.95	0.0333
CO_2-water	142.0	0.0162	166.55/2 = 83.27	0.0911
CO_2-ethanol	123.8	0.0320	215.32/2 = 107.66	0.0263

*Value adopted from H_2S-ethanol.

Many literature studies report a relatively strong hydrogen bonding interaction between H_2S and water or low molecular weight alcohols. If such cross-associating interactions are accounted for, the CPA model results in very satisfactory correlations for the phase behavior (vapor- and liquid-liquid equilibria) of H_2S-water and for the vapor-liquid equilibria of H_2S-methanol systems. Calculations for mixtures of H_2S with glycols are in satisfactory agreement with experimental data, even when H_2S is treated as nonassociating fluid. Assuming solvation of H_2S in glycols (i.e., assuming that H_2S has only proton donor sites that are able to cross associate with glycol molecules) improves calculations only for the H_2S-MEG mixture.

Using interaction parameters obtained solely from binary systems, CPA can predict satisfactorily phase equilibria of one ternary and three quaternary H_2S-containing systems. The best results are obtained when the solvation between H_2S and water or methanol is explicitly accounted for (as well as for CO_2-water), especially when the cross-association energy is taken from experimental spectroscopic studies. However, equally good results are obtained when a self-associating H_2S molecule is assumed (using the 3B association scheme), when the cross-association energy, which characterizes its interactions with polar molecules, is taken from experimental spectroscopic studies.

Table 21. Kamlet-Taft Solvatochromic Parameters for Compounds Considered in this Work[50]

Compound	Base Parameter (β)	Acid Parameter (a)
Methanol	0.62	0.93
Ethanol	0.77	0.83
MEG	0.52	0.90
Water	0.18	1.17
H_2S	–	–

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Notation

b = CPA fluid specific parameter
c_1 = CPA fluid specific parameter
$g(\rho)$ = radial distribution function
k_{ij} = binary interaction parameter
n = reduced density
P = pressure
P^{sat} = vapor pressure
R = gas constant
T = temperature
T_c = critical temperature
T_{melt} = melting point
T_r = reduced temperature
X_{A_i} = fraction of free sites of type A belonging to molecule i
x_i, y_i = mole fraction of component i (liquid and vapor, respectively)
V_m = molar volume

Greek letters

α = CPA energy parameter
α_o = fluid specific parameter
$\beta^{A_iB_j}$ = association volume for the hydrogen bond between sites A and B belonging in molecules i and j, respectively
β_{cross} = cross-association volume
$\Delta^{A_iB_j}$ = association strength between two sites A and B belonging to molecules i and j, respectively
$\varepsilon^{A_iB_j}$ = association energy for the hydrogen bond between sites A and B belonging to molecules i and j, respectively
ε_{cross} = cross-association energy
ρ = density
ρ^{liq} = density of saturated liquid phase

Literature Cited

1. Carroll JJ, Mather AE. A generalized correlation for the Peng-Robinson interaction coefficients for paraffin hydrogen sulfide binary systems. *Fluid Phase Equilib.* 1995;105:221–228.
2. Stamataki S, Magoulas K. Prediction of phase equilibria and volumetric behavior of fluids with high concentration of hydrogen sulfide. *Oil Gas Sci Technol.* 2000;55:511–522.
3. Barreau A, Blanchon le Bouhelec E, Habchi Tounsi KN, Mougin P, Lecomte F. Absorption of H_2S and CO_2 in alkanolamine aqueous solution: experimental data and modelling with the electrolyte-NRTL model. *Oil Gas Sci Technol.* 2006;61:345–361.
4. Ungerer P, Lachet V, Tavitian B. Applications of molecular simulation in oil and gas production and processing. *Oil Gas Sci Technol.* 2006;61:387–403.
5. Cabaleiro-Lago EM, Rodrıguez-Otero J, Pena-Gallego A. Computational study on the characteristics of the interaction in naphthalene. $(H_2X)_{n=1,2}$ (X = O, S). *Clusters J Phys Chem A.* 2008;112:6344–6350.
6. Pecul K. Study of the hydrogen bond and of the proton transfer between two H_2S molecules. *Theoret Chim Acta (Bed).* 1977;44:77–83.
7. Sennikov PG, Shkrunin VE, Tokhadze KG. Intermolecular interactions of hydrogen sulfide and hydrogen selenide with some proton donors and proton acceptors in liquid phase. *J Molec Liquids*. 1990; 46:29–38.
8. del Bene JE. Ab initio molecular orbital study of the structures and energies of neutral and charged bimolecular complexes of H_2O with the hydrides AH_n (A= N, O, F, P, S, and Cl). *J Phys Chem.* 1988; 92:2874–2880.
9. Novaro O, Les A, Galvan M, del Conde G. Theoretical study of three-body nonadditive interactions for the H_2S-$(H_2O)_2$ system. *Theoret Chim Acta (Ber).* 1983;64:65–81.
10. Les A. A pseudopotential study if the hydrogen bond in $H_2O.H_2S$, H_2SH_2S and H_2OH_2Se systems. *Theoret Chim Acta (Ber).* 1985;66:375–393.
11. Sennikov PG, Shkrunin VE, Raldugin DA, Tokhadze KG. Weak hydrogen bonding in ethanol and water solutions of liquid volatile inorganic hydrides of group IV-VI elements (SiH_4, GeH_4, PH_3, AsH_3, H_2S, and H_2Se) 1 IR spectroscopy of H bonding in ethanol solutions in hydrides. *J Phys Chem.* 1996;100:6415–6420.
12. Ruffine L, Mougin P, Barreau A. How to represent hydrogen sulfide within the CPA equation of state. *Ind Eng Chem Res.* 2006;45: 7688–7699.
13. Kontogeorgis GM, Folas GK, Muro-Suñé N, Roca Leon F, Michelsen ML. Solvation phenomena in association theories with applications to oil and gas and chemical industries. *Oil Gas Sci Technol - Rev IFP*. 2008;63:305–319.
14. Perfetti E, Thiery R, Dubessy J. Equation of state taking into account dipolar interactions and association by hydrogen bonding. I. Application to pure water and hydrogen sulfide. *Chem Geol.* 2008;251:58–66.
15. Perfetti E, Thiery R, Dubessy J. 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. *Chem Geol.* 2008;251:50–57.
16. Gubbins KE, Twu CH. Thermodynamics of polyatomic fluid mixtures-1 theory. *Chem Eng Sci.* 1978;33:863–878.
17. Li Z, Firoozabadi A. Cubic-plus-association equation of state for water-containing mixtures: is "cross association" necessary? *AIChE J*. 2009;55:1803–1813.
18. Carroll JJ, Mather AE. The correlation of the vapor-liquid equilibrium in hydrogen sulfide—paraffin hydrocarbons using the Peng-Robinson equation. *Fluid Phase Equilib.* 1995;112:167–168.
19. Moysan JM, Paradowski H, Vidal J. Prediction of phase behaviour of gas-containing systems with cubic equations of state. *Chem Eng Sci*. 1986;41:2069–2074.
20. Prausnitz JM, Tavares FW. Thermodynamics of fluid-phase equilibria for standard chemical engineering operations. *AIChE J*. 2004;50:739–761.
21. Carroll JJ, Mather AE. Phase equilibrium in the system water-hydrogen sulphide. Modelling the phase behavior with an equation of state Canadian. *J Chem Eng*. 1989;67:999–1003.
22. Spiliotis N, Boukouvalas C, Tzouvaras N, Tassios D. Application of the LCVM model to multicomponent systems: extension of the UNIFAC interaction parameter table and prediction of the phase behavior of synthetic gas condensate and oil systems. *Fluid Phase Equilib.* 1994;101:187–210.
23. Ahlers J, Gmehling J. Development of a universal group contribution equation of state. II. Prediction of vapor-liquid equilibria for asymmetric systems. *Ind Eng Chem Res.* 2002;41:3489–3498.
24. Ahlers J, Gmehling J. Development of a universal group contribution equation of state. III. Prediction of vapor-liquid equilibria, excess enthalpies, and activity coefficients at infinite dilution with the VTPR model. *Ind Eng Chem Res.* 2002;41:5890–5899.
25. Holderbaum T, Gmehling J. PSRK: a group contribution equation of state based on UNIFAC. *Fluid Phase Equilib.* 1991;70:251–265.
26. Chen J, Fischer K, Gmehling J. Modification of PSRK mixing rules and results for vapor-liquid equilibria, enthalpy of mixing and activity coefficients at infinite dilution. *Fluid Phase Equilib.* 2002;200: 411–429.
27. Kontogeorgis GM, Voutsas EC, Yakoumis IV, Tassios DP. An equation of state for associating fluids. *Ind Eng Chem Res.* 1996;35: 4310–4318.
28. Kontogeorgis GM, Michelsen ML, Folas GK, Derawi S, von Solms N, Stenby EH. Ten years with the CPA (cubic-plus-association) equation of state. I. Pure compounds and self-associating systems. *Ind Eng Chem Res.* 2006;45:4855–4868.
29. Kontogeorgis GM, Michelsen ML, Folas GK, Derawi S, von Solms N, Stenby EH. Ten years with the CPA (cubic-plus-association) equation of state. II. Cross-associating and multicomponent systems. *Ind Eng Chem Res.* 2006;45:4869–4878.
30. Huang SH, Radosz M. Equation of state for small, large, polydisperse and associating molecules. *Ind Eng Chem Res.* 1990;29:2284–2294.
31. *DIPPR DIADEM- The DIPPR Interface and Data Evaluation Manager for the Design, Institute for Physical Properties*, 2006, Brigham Young University-Thermophysical Properties Laboratory, Version 1.1.0. (Computer Program).
32. Derawi SO, Michelsen ML, Kontogeorgis GM, Stenby EH. Application of the CPA equation of state to glycol/hydrocarbons liquid-liquid equilibria. *Fluid Phase Equilib.* 2003;209:163–184.
33. Folas GK, Kontogeorgis GM, Michelsen ML, Stenby EH. Application of the cubic-plus-association equation of state to mixtures with polar chemicals and high pressures. *Ind Eng Chem Res.* 2006;45: 1516–1526.
34. Folas GK, Kontogeorgis GM, Michelsen ML, Stenby EH. Application of the cubic-plus-association (CPA) equation of state to complex mixtures with aromatic hydrocarbons. *Ind Eng Chem Res.* 2006;45:1527–1538.
35. Wormald CJ, Colling CN, Sellars AJ. Thermodynamic properties of gaseous mixtures containing water, In: Hirsch LH. *Proceedings of the International Gas Research Conference*, Rockville: Government Institutes Inc., 1983:1070–1079.
36. Selleck FT, Carmichael LT, Sage BH. Phase behavior in hydrogen sulfide—water system. *Ind Eng Chem.* 1952:44;2219–2226.
37. Gillespie PC, Wilson GM. *Research Report GPA-RR-48*. Gas Processors Association, UT, 1982.
38. Leu A-D, Carroll JJ, Robinson DB. The equilibrium phase properties of the methanol-hydrogen sulfide binary system. *Fluid Phase Equilib.* 1992;72:163–172.
39. Jou F-Y, Deshmukh RD, Otto FD, Mather AE. Vapor-liquid equilibria of H_2S and CO_2 and ethylene glycol at elevated pressures. *Chem Eng Commun.* 1990;87:223–231.
40. Jou F-Y, Otto FD, Mather AE. Solubility of H_2S and CO_2 in diethylene glycol at elevated pressures. *Fluid Phase Equilib.* 2000;175:53–61.
41. Jou F-Y, Deshmukh RD, Otto FD, Mather AE. Vapor-liquid equilibria for acid gases and lower alkanes in triethylene glycol. *Fluid Phase Equilib.* 1987;36:121–140.
42. Bierlein JA, Kay WB. Phase-equilibrium properties of system carbon dioxide-hydrogen sulfide. *Ind Eng Chem.* 1953;45:618–624.
43. Reamer HH, Sage BH, Lacey WN. Phase equilibria in hydrocarbon systems. *Ind Eng Chem Res.* 1951;43:976–981.
44. Kaira H, Robinson DB, Krishnan TR. The equilibrium phase properties of the ethane-hydrogen sulfide at subambient temperatures. *J Chem Eng Data.* 1977;22:85–88.

45. Brewer J, Rodewald N, Kurata F. Phase equilibria of the propane-hydrogen sulfide system from cricondontherm to the solid-liquid-vapor region. *AIChE J*. 1961;7:13–16.
46. Leu A-D, Robinson DB. Equilibrium phase properties of the n-butane-hydrogen sulfide and isobutane-hydrogen sulfide binary systems. *J Chem Eng Data*. 1989;34:315–319.
47. Hensel WE Jr, Massoth FE. Phase equilibria for the ternary system: CH_4-CO_2-H_2S at low temperatures. *J Chem Eng Data*. 1964;9:352–356.
48. Ng H-J, Chen C-J. *Research Report GPA-RR-149*. Gas Processors Association and Gas Research Institute, Edmonton, 1995.
49. Huang SS, Leu A-D, Ng H-J, Robinson DB. The phase behavior of two mixtures of methane, carbon dioxidem hydrogen sulfide and water. *Fluid Phase Equilib*. 1985;19:21–32.
50. Kamlet MJ, Abboud JM, Abraham MH, Taft RW. Linear Solvation Energy Relationships. 23. A comprehensive Study of the Solvatochromic Parameters π^*, α, and β, and Some Methods for Simplifying the Generalized Solvatochromic Equation. *J Org Chem*. 1983; 48:2877–2887.
51. Knudsen K, Stenby EH, Fredenslund Aa. A comprehensive comparison of mixing rules for calculation of phase equilibria in complex systems. *Fluid Phase Equilib*. 1993;82:361–368.
52. Vafaie-Sefti M, Modarress H, Meibodi ME, Mousavi-Dehghani SA. Association equation of state for hydrogen-bonded substances. *Can J Chem Eng*. 2007;85:65–74.

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