



# Modeling of gas solubility in brine

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## Abstract

Cubic equations of state (EOS) are widely used to represent the phase behavior of gas–oil-systems, whereas different types of models have traditionally been used to describe gas solubility in aqueous mixtures. Since formation water is often produced together with gas and oil, it is also desirable to model gas solubility in formation water using an EOS. It has previously been shown that the mutual solubility of hydrocarbons and pure water can be well represented by a cubic EOS by applying a non-classical mixing rule for the  $a$ -parameter. However, formation water produced together with gas and oil will often have a considerable content of salts, which must be accounted for in gas solubility calculations. It is shown that the mixing rule of Huron and Vidal can be stretched to account for the presence of the salts NaCl, KCl and CaCl<sub>2</sub> in the water phase. This is done by assigning hypothetical critical properties to the salts, and estimating interaction parameters for gas-salt interactions based on experimental gas solubility data. This model concept gives a fair representation of the gas solubility in salt water. © 2002 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

The brine produced with gas and oil plays an important role in the design of transport and separation equipment. When both water and light hydrocarbons are present at low temperatures there is a potential risk of gas hydrate formation. Other potential problems are related to water contained in gas that is produced in a separation plant. The water may condense at a later stage. More recently the gas solubility in water has become an important issue because of restrictions on the hydrocarbon content in water to be disposed. To evaluate the problems related to the produced formation water, it is desirable to have a versatile thermodynamic model capable of representing the mutual solubility of gas–oil–water systems. Because the formation water often has a considerable salt content, such a model must be capable of accounting for the influence of salts in solution on gas solubility and on the volatility of the water. The salts are known to lower the gas solubility significantly. Salts are also known to act as anti-freeze, which affects hydrate formation.

A reliable model for the gas solubility in salt water will also be valuable when evaluating fluid inclusions

with water. The water phase trapped in the inclusion was saturated with gas components at trapping conditions. The pressure needed to dissolve the gas in the water phase in the inclusion therefore provides information about the trapping pressure. Since the water contains salts, accurate modeling of the solubility of light hydrocarbon gases in salt water is a prerequisite for obtaining a reasonably constrained set of trapping conditions.

## 2. Models

### 2.1. Equations of state in classical form

Gas–oil phase equilibria can be well represented using cubic EOS's. Two of the most popular cubic EOS's are the Soave–Redlich–Kwong (SRK) (Soave, 1972) and the Peng Robinson (PR) (Peng and Robinson, 1976) equations. The SRK equation with the volume translation extension of Peneloux et al. (1982) is presented in Appendix. Cubic EOS's were originally intended for use primarily on hydrocarbon mixtures, for which type of mixtures the binary interaction parameter ( $k_{ij}$ ) entering into the expression for the  $a$ -parameter (Equation (A10)) is zero or close to zero. Slightly polar components like N<sub>2</sub> and CO<sub>2</sub> can be handled by applying binary interaction parameters of the order of 0.1 for

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**Nomenclature**

<i>a</i>	EOS parameter
<i>b</i>	EOS parameter
<i>c</i>	Peneloux volume correction parameter
EOS	Equation of state
$G_{\infty}^E$	Excess Gibbs energy at infinite pressure
$g_{ij}$	Binary interaction parameter in HV mixing rule
HV	Huron and Vidal
<i>i</i>	Component index
<i>j</i>	Component index
$k_{ij}$	Binary interaction parameter in the classical SRK mixing rule
<i>m</i>	Function of acentric factor
<i>P</i>	Pressure
PR	Peng–Robinson
<i>R</i>	Gas constant
SRK	Soave–Redlich–Kwong
<i>V</i>	Molar volume
<i>z</i>	Mole fraction

*Subscripts and superscripts*

<i>c</i>	Critical property
<i>V</i>	Vapor phase

*Symbols*

$\alpha$	Temperature dependent part of parameter <i>a</i> in EOS
$\alpha_{ij}$	Non-randomness parameter in HV mixing rule
$\omega$	Acentric factor
$\Omega_a$	Parameter in EOS
$\Omega_b$	Parameter in EOS
$\varphi$	Fugacity coefficient
$\tau$	Parameter in HV mixing rule

N<sub>2</sub>/CO<sub>2</sub>-hydrocarbon pairs. Several attempts have been made to extend the application area for cubic EOS's to also cover hydrocarbon–water mixtures. The simplest approach is to use binary interaction parameters ( $k_{ij}$ ) in the order of 0.5 for hydrocarbon–water pairs, resulting in virtually no solubility. This is not generally satisfactory. For most conditions it will underestimate gas solubility in water.

### 2.2. Activity coefficient models

Vapor–liquid equilibria for mixtures of polar sub-critical compounds can be well represented at low pressures through the modified Raoult's law

$$y_i P = \gamma_i x_i P_i^{\text{sat}} \quad (1)$$

where *P* is the pressure,  $y_i$  is the mole fraction of component *i* in the vapor phase and  $x_i$  the mole fraction of component *i* in the liquid phase.  $\gamma_i$  is the activity coefficient of component *i* in the liquid phase and  $P_i^{\text{sat}}$  the vapor pressure of component *i* at the current temperature. Raoult's law assumes the gas phase to be ideal. It can be modified to take into consideration non-idealities in the gas phase by multiplying the left-hand side of the equation by the fugacity coefficient ( $\varphi_i^V$ ) of component *i* in the vapor phase.  $\gamma_i$  may be calculated from an activity coefficient model as for example UNIFAC (Fredenslund et al., 1975), UNIQUAC (Abrams and Prausnitz, 1975) or NRTL (Renon and Prausnitz, 1968). Activity coefficient models may be extended to include an additional electrostatic term (e.g. Sander et al., 1986; Thomsen and Rasmussen, 1999) accounting for the possible presence of salts.

The concept of activity coefficients in its original form is limited to sub-critical components. A component like methane at the conditions of relevance to gas and oil production is above its critical point, and therefore it is impossible to evaluate  $P_i^{\text{sat}}$ . Various approaches have been tried to overcome this problem, including attempts to extrapolate the vapor pressure curve. None of these approaches are completely satisfactory in an oil–gas production context.

### 2.3. EOS based models

The classical mixing rule for the *a*-parameter of the SRK and PR EOS's is shown as Eq. (A8) in the Appendix. This mixing rule is well suited for hydrocarbon mixtures. Using an appropriate binary interaction parameter it is also applicable to mixtures of hydrocarbons with a minor content of inorganic gases, such as nitrogen or carbon dioxide. The binary interaction parameter  $k_{ij}$  is symmetrical, meaning that  $k_{ij} = k_{ji}$ . It is thereby assumed that any fluid phase is homogeneous in the sense that the composition in any fluid segment equals the overall composition. In other words the molecules in each phase are assumed to be randomly distributed. This is a good assumption for mixtures of non-polar components as for example gas and oil mixtures. In a water phase with dissolved gases, the assumption is not valid due to differences in polarity between water and the gas molecules. This is the main reason why the classical mixing rule for the *a*-parameter as presented in the Appendix is insufficient for hydrocarbon–water mixtures.

Huron and Vidal (1979) proposed a model concept combining the original SRK equation with the NRTL activity coefficient model. This led to a new mixing rule for the *a*-parameter, as presented in the Appendix.

The classical binary interaction parameter  $k_{ij}$  is replaced by three parameters

- $\alpha_{ij}$ , which is a non-randomness parameter;
- $g_{ij}$ , which accounts for the molecular interactions when molecules of type  $i$  are surrounded by molecules of type  $j$ .
- $g_{ji}$ , which accounts for the molecular interactions when molecules of type  $j$  are surrounded by molecules of type  $i$ .

The  $g$ -parameters can be interpreted as a non-symmetrical  $k_{ij}$ . By using the Huron and Vidal mixing rule for the  $a$ -parameter it is possible to describe phase equilibria of mixtures of hydrocarbons, water and fluid hydrate inhibitors such as methanol and glycol (Kristensen et al., 1993; Pedersen et al., 1996).

The presence of salts introduces electrostatic interactions in the water phase. Aasberg-Petersen et al. (1991) and Tohidi et al. (1994) have proposed to model the electrostatic forces by adding a modified Debye–Hückel term to the traditional EOS concept when calculating the fugacity of water. Salts are assumed not to distribute between gas, oil and water, but only to be present in the water. The electrolytes (salts) do not, therefore, have to be dealt with directly. If salts are not present, the model reduces to the classical EOS. Søreide and Whitson (1992) have proposed an approach based on the Peng–Robinson equation. The temperature dependent term in the EOS ( $\alpha$ ) is usually a function of the reduced temperature ( $T/T_c$ ) and the accentric factor. For water this term is modified, and the modification is a function of the amount of salt in solution. The gas solubility calculated from the PR EOS is further corrected using an empirical correction factor.

#### 2.4. Choice of model

In our approach, salts are modeled as hypothetical components with hypothetical critical properties. In the water phase each salt molecule is assumed to split into as many molecules as the number of ions formed when the actual salt dissociates in aqueous solution. The hypothetical critical properties are for the split molecules. The Huron and Vidal (HV) mixing rule is used for gas–water, water–salt and gas–salt binaries. This is an attractive approach because the conventional EOS thermodynamic routines can still be used. The HV mixing rule further has the advantage that it reduces to the classical mixing rule in the absence of components requiring the advanced mixing rule. Therefore, there is no need to estimate HV interaction parameters for hydrocarbon–hydrocarbon binaries. Due to its simplicity, the above considerations have taken precedence over models designed for electrolyte containing systems.

What is needed to handle salts within the selected model concept is to determine appropriate hypothetical critical properties of the salt components and to estimate gas–water, water–salt and gas–salt HV interaction parameters.

The parameters to be estimated must fulfil the following criteria

- the hypothetical salt components must be (almost) involatile;
- the freezing point depression of the water due to the presence of salts should be represented accurately;
- the effect of salts on the gas solubility in water should be well represented.

The salts to be considered are NaCl, KCl and CaCl<sub>2</sub> since they are normally the most abundant in reservoir brine.

#### 2.5. Handling dissolved salts

Salts dissociate into ions when dissolved in water. NaCl will for example split up into a Na<sup>+</sup> ion and a Cl<sup>−</sup> ion. In actual practice, each NaCl is treated as two hypothetical molecules (one Na<sup>+</sup> and one Cl<sup>−</sup>). These two hypothetical molecules are both assumed to have the properties given in Table 1. Similarly KCl is treated as 2 and CaCl<sub>2</sub> as 3 hypothetical molecules, the properties of which are also given in Table 1. To the model, salts appear as ordinary molecules present in amounts 2 or 3 times their amount in undissociated form.

Dissolved salts will remain in the water phase. The critical properties in Table 1 are close to those of triethylene glycol (TEG). TEG has a similar effect on water as salts in terms of freezing point depression and salting out of hydrocarbons. TEG further has low volatility and low solubility in liquid hydrocarbons. To make sure the salts are involatile and insoluble in hydrocarbons, large fugacity coefficients are assigned to the salt components in the gas and oil phases.

The presence of salts has two effects on the H<sub>2</sub>O molecules in the water phase. It lowers the H<sub>2</sub>O mole fraction and fugacity coefficient. The first term depends on the amount of salt and on the number of ions formed when the salt dissociates, whereas the second term depends on the H<sub>2</sub>O–salt interactions. NaCl will, for example, split into Na<sup>+</sup> and Cl<sup>−</sup>, and the dilution effect of NaCl will be twice the number of undissociated NaCl molecules. CaCl<sub>2</sub> is represented as 3 molecules. Each Ca<sup>2+</sup> ion is further assumed to have 6 H<sub>2</sub>O-molecules

Table 1  
Hypothetical properties of salts

Salt	$T_c$ K	$P_c$ atm	$\omega$	Molecules per salt	No. of crystal water molecules
NaCl	700	35	1.0	2	0
KCl	800	35	1.0	2	0
CaCl <sub>2</sub>	800	35	1.0	3	6

associated with it, which reduces the number of free H<sub>2</sub>O-molecules. Imagine a system consisting of 100 mol of H<sub>2</sub>O. Add 1 mol of CaCl<sub>2</sub>. According to the model the CaCl<sub>2</sub> will associate with 6 mol of H<sub>2</sub>O and split into 3 mol of salt irrespective of temperature and pressure. The model sees 94 mol of H<sub>2</sub>O and 3 mol of salt. The

Ca<sup>2+</sup>-H<sub>2</sub>O association is similar to the CaCl<sub>2</sub> crystal water bonds acting in the solid state. The chosen formulation implies that partially dissociated salts cannot be handled. Salts where one or both ions participate in acid-base equilibria cannot be handled rigorously.

Table 2

Ranges for experimental data and average absolute deviations for HC-H<sub>2</sub>O-systems

System H <sub>2</sub> O and	<i>T</i> <sub>min</sub> K	<i>T</i> <sub>max</sub> K	<i>P</i> <sub>min</sub> atm	<i>P</i> <sub>max</sub> atm	Abs. dev.% HV	Ref. exp. data <sup>a</sup>
N <sub>2</sub>	273.15	442.15	0.7	1000.0	9.9	1,2,3
CO <sub>2</sub>	348.15	623.15	16.0	1400.0	37.0	4,5
C <sub>1</sub>	298.15	444.15	40.0	608.0	26.4	1,6
C <sub>2</sub>	303.15	523.15	1.0	2000.0	25.0	7
C <sub>3</sub>	278.15	344.15	1.0	26.0	42.1	8
iC <sub>4</sub>	278.15	318.15	1.0	1.0	16.4	8
nC <sub>4</sub>	273.15	353.15	1.0	1.0	19.3	8

<sup>a</sup> Refs: 1: O'Sullivan and Smith (1970), 2: Smith et al. (1962), 3: Solubility Data Series (1982b), 4: Prutton and Savage, (1945) 5: Takenouchi and Kennedy (1965), 6: Solubility Data Series (1972), 7: Solubility Data Series (1982a), 8: Solubility Data Series (1982b).

Table 3

Ranges for experimental data and average absolute deviations for gas-H<sub>2</sub>O-salt systems. *S* is salinity

System H <sub>2</sub> O and	<i>T</i> <sub>min</sub> K	<i>T</i> <sub>max</sub> K	<i>P</i> <sub>min</sub> atm	<i>P</i> <sub>max</sub> atm	<i>S</i> <sub>min</sub> (wt.%)	<i>S</i> <sub>max</sub> (wt.%)	Abs. dev.% Classic	Abs. dev.% HV	Ref. to exp. data <sup>a</sup>
<i>NaCl and</i>									
N <sub>2</sub>	285.75	398.15	1.0	608.0	5.5	26.6	47.4	8.7	1,2,3
CO <sub>2</sub> (aq)	298.15	523.15	1.0	1382.0	2.6	25.0	44.1	20.3	4,5,6
C <sub>1</sub>	283.15	398.15	1.0	608.0	1.4	20.3	48.0	25.4	1,3,7
C <sub>2</sub>	273.15	303.15	1.0	16.0	1.4	10.9	20.8	14.3	3,7,8
C <sub>3</sub>	264.65	344.85	0.1	1.0	1.4	26.0	29.1	9.6	3,9
nC <sub>4</sub>	263.85	344.85	0.6	1.0	3.5	21.3	41.5	31.3	3,9,10
<i>KCl and</i>									
N <sub>2</sub>	273.15	513.15	96.8	96.8	3.7	13.9	44.3	13.2	11
CO <sub>2</sub> (aq)	298.15	308.15	1	1.8	2.6	26.4	39.1	3.2	5,6
C <sub>1</sub>	288.15	303.15	1.0	200.0	3.6	23.2	14.3	7.4	7,12
C <sub>2</sub>	283.15	303.15	1.0	1.0	7.2	7.2	12.3	0.0	7
C <sub>3</sub>	298.15	298.15	1.0	1.0	1.9	10.6	7.7	4.4	9
nC <sub>4</sub>	285.75	344.85	1.0	1.0	7.0	7.0	16.6	8.3	3
<i>CaCl<sub>2</sub> and</i>									
N <sub>2</sub>	303.15	303.15	12.2	75.0	5.3	43.3	44.1	36.4	2
CO <sub>2</sub> (aq)	298.15	394.15	1.0	703.0	2.5	37.0	38.7	16.9	5,13
C <sub>1</sub>	298.15	398.15	8.0	600.0	2.7	35.7	54.0	21.4	12,14
C <sub>2</sub>	273.15	273.15	1.0	16.0	5.3	14.8	8.8	8.6	8

<sup>a</sup> Refs: 1: O'Sullivan and Smith (1970), 2: Smith et al. (1962), 3: Morrison and Billett (1952), 4: Takenouchi and Kennedy (1965), 5: Yasunishi and Yoshida (1979), 6: Anon. (1973), 7: Ben-Naim and Yaacobi (1974), 8: Solubility Data Series (1982a), 9: Solubility Data Series (1982b), 10: Rice et al. (1976), 11: Solubility Data Series (1982b), 12: Solubility Data Series (1987), 13: Prutton and Savage (1945), 14: Blanco and Smith (1978).

### 3. Experimental data

A prerequisite for accurate modeling of the gas solubility in salt water is an accurate modeling of the gas solubility in pure water. It has previously (Pedersen et al., 1996) been shown that this can be accomplished using the HV mixing rule for gas-water interactions. Table 2 gives references to experimental data for the solubilities of gas components in water.

Table 3 gives an overview of the experimental data used for the solubility of the gas components N<sub>2</sub>, CO<sub>2</sub> (as CO<sub>2</sub>(aq)), C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and nC<sub>4</sub> in water containing each of the salts, NaCl, KCl and CaCl<sub>2</sub>.

#### 3.1. Parameter estimation

The HV interaction parameters used for H<sub>2</sub>O-gas interactions are shown in Table 4. Based on freezing

Table 4  
HV interaction parameters H<sub>2</sub>O (1)–gas (2)

Gas	$\alpha_{12}$	$(g_{21}-g_{11})/R$ (K)	$(g_{12}-g_{22})/R$ (K)
N <sub>2</sub>	0.0768	–388	4911
CO <sub>2</sub> (aq)	0.0144	–4676	5119
C <sub>1</sub>	0.122	274	2467
C <sub>2</sub>	0.122	274	2467
C <sub>3</sub>	0.122	274	2467
iC <sub>4</sub>	0.145	681	2507
nC <sub>4</sub>	0.145	681	2507

Table 5  
HV interaction parameters H<sub>2</sub>O (1)–salt (2)

	$\alpha_{12}$	$(g_{21}-g_{11})/R$ (K)	$(g_{12}-g_{22})/R$ (K)
NaCl	–0.7335	–11.70	95.12
KCl	–0.8262	650.8	92.26
CaCl <sub>2</sub>	–2.104	170.5	66.88

point depression data, HV parameters have been estimated for NaCl–H<sub>2</sub>O, KCl–H<sub>2</sub>O and CaCl<sub>2</sub>–H<sub>2</sub>O interactions. The salts are treated as described in the section on handling of dissolved salts. The interaction parameters estimated are shown in Table 5.

Two sets of binary interaction parameters have been estimated for gas–salt interactions.

- binary interaction parameters ( $k_{ij}$ ) in the classical mixing rule;
- HV binary interaction parameters ( $\alpha_{ij}$ ,  $g_{ij}$  and  $g_{ji}$ ).

In general it is to be expected that the better representation of the gas solubility will be achieved using the HV mixing rule. It takes into account non-random component distributions, and it presents 3 interaction

Table 6  
Interaction parameters ( $k_{ij}$ ) in classical mixing rule

	N <sub>2</sub>	CO <sub>2</sub> (aq)	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	nC <sub>4</sub>
NaCl	3.20	2.10	2.02	0.78	0.72	0.70
KCl	5.24	1.79	1.64	1.33	1.36	1.35
CaCl <sub>2</sub>	2.29	2.23	2.07	1.18	–	–

Table 7  
 $\alpha_{ij}$  values for use with HV model

	N <sub>2</sub>	CO <sub>2</sub> (aq)	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	nC <sub>4</sub>
NaCl	0.0105	–0.0070	0.0840	0.0620	0.0592	0.0369
KCl	0.0078	–0.1218	0.0970	0.0210	0.0441	0.0078
CaCl <sub>2</sub>	0.0174	–0.1110	0.0550	0.0364	–	–

Table 8  
 $(g_{21}-g_{11})/R$  values for use with HV model. 1 = gas, 2 = salt. Values in K

	N <sub>2</sub>	CO <sub>2</sub> (aq)	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	nC <sub>4</sub>
NaCl	1773	3087	5281	4227	4777	3528
KCl	2335	1137	4007	50127	7499	35311
CaCl <sub>2</sub>	2200	1721	14765	3080	–	–

Table 9  
 $(g_{12}-g_{22})/R$  values for use with HV model. 1 = gas, 2 = salt. Values in K

	N <sub>2</sub>	CO <sub>2</sub> (aq)	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	nC <sub>4</sub>
NaCl	94947	0	7623	12235	10539	20193
KCl	41212	1865	6733	24788	60604	–48374
CaCl <sub>2</sub>	80541	628	8790	99000	–	–

parameters against only one in the classical mixing rule. This provides more flexibility. On the other hand for some gas–salt pairs the data material is quite limited. Therefore, for each binary we evaluate whether the available gas solubility data can be represented equally well or almost as well using the classical mixing rule.

The estimated binary interaction parameters are shown in Tables 6–9.

#### 4. Results

Fig. 1 illustrates the improvement obtained by using the HV model relative to the original SRK. The figure shows the solubility of methane in pure water.

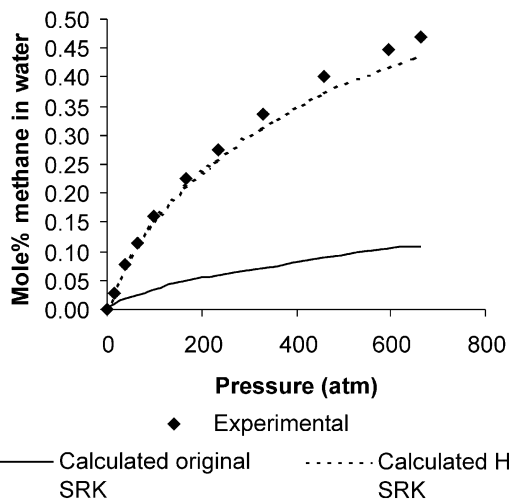


Fig. 1. Solubility of methane in pure water at 310.95 K.

Table 3 shows the average deviation between the experimental and calculated solubilities for the considered gas–water–salt systems. For all binaries the results obtained with the HV model are better than or equally good as those obtained with the classical model. However, for some systems the temperature and/or pressure ranges used are quite narrow compared to the ranges of interest—approximately 273–433 K and 1–500 atm. In those cases, use of the classical model is preferred to the HV model. The HV mixing rule includes an exponential temperature dependent term and may potentially extrapolate to unrealistic interaction energies outside the temperature range covered by experimental data. For the system  $\text{CO}_2(\text{aq})\text{--H}_2\text{O--KCl}$ , the HV model is still recommended, even though the experimental data only cover a temperature range of 10 K. This exception is made because the results obtained with the HV mixing rule are of a much higher quality than those obtained with the classical mixing rule. Table 10 shows the model preferred for each system.

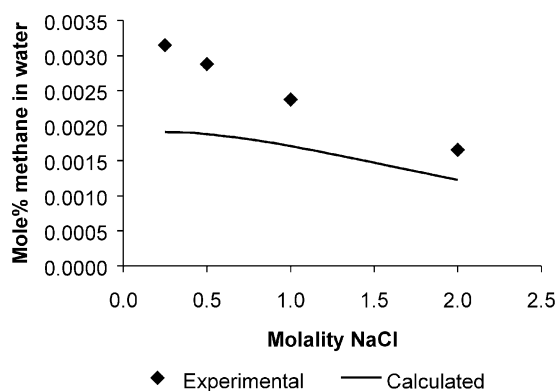


Fig. 2. Solubility of methane in NaCl containing water at 1 atm and 283.15 K.

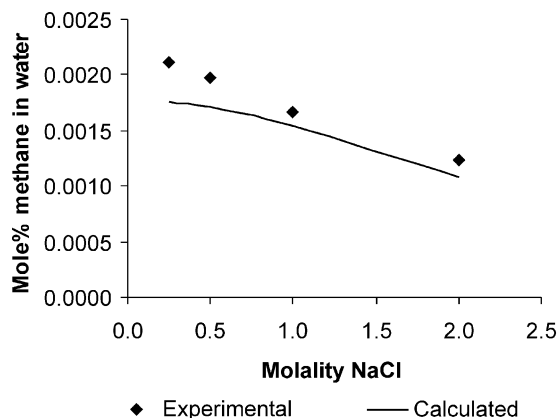


Fig. 3. Solubility of methane in NaCl containing water at 1 atm and 303.15 K.

Figs. 2 and 3 exemplify the accuracy obtained for the solubility of methane in water with NaCl at two different temperatures. A molality of 2 for NaCl corresponds to approximately 11 wt.%. Somewhat better results are obtained for a temperature of 303.15 K than for a temperature of 283.15 K. Fig. 4 exemplifies the accuracy obtained for the solubility of methane in water with dissolved  $\text{CaCl}_2$ . A molality of 2 of  $\text{CaCl}_2$  corresponds to approximately 20 wt.%.

## 5. Conclusions

The Soave–Redlich–Kwong EOS may be used to represent phase equilibria between hydrocarbon mixtures and salt water, if the non-classical mixing rule of Huron and Vidal is used for the parameter  $a$  in the EOS. The salts are treated as hypothetical components with well defined critical properties. Water–salt interaction parameters have been estimated using freezing point depression data. Gas–water and gas–salt interaction parameters have been estimated from gas solubility data in pure water and in salt water. For some gas–salt binaries the extent of the experimental data material does not justify estimation of the 3 interaction parameters entering into the HV mixing rule. For these systems we recommend using the classical mixing rule with an appropriate  $k_{ij}$ . The experimental gas solubility data can in general be matched with an error less than 25%.

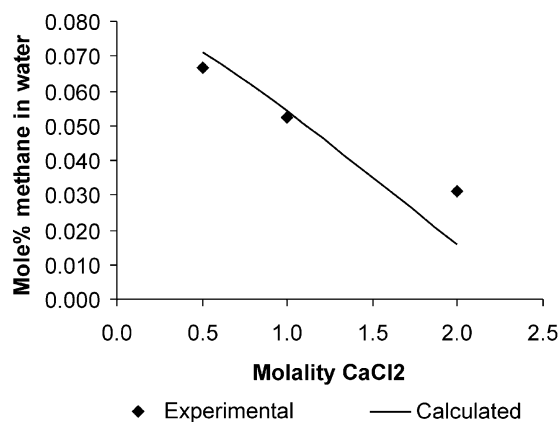


Fig. 4. Solubility of methane in  $\text{CaCl}_2$  containing water at 37.4 atm and 298.15 K.

Table 10  
Recommended mixing rule

	$\text{N}_2$	$\text{CO}_2(\text{aq})$	$\text{C}_1$	$\text{C}_2$	$\text{C}_3$	$n\text{C}_4$
NaCl	HV	HV	HV	Classic	Classic	Classic
KCl	HV	HV	Classic	Classic	Classic	Classic
$\text{CaCl}_2$	Classic	HV	HV	Classic	No data	No data

## Appendix

The SRK equation with the Peneloux volume extension takes the form

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+c)(V+b+2c)} \quad (\text{A1})$$

$R$  is the universal gas constant, which has a known value.  $P$  is the pressure,  $T$  the absolute temperature,  $V$  the molar volume and  $a$  and  $b$  are EOS parameters. For a pure component the parameter  $a$  is found from

$$a(T) = a_c(T) \quad (\text{A2})$$

where

$$a_c = \Omega_a \frac{R^2 T_c^2}{P_c} \quad (\text{A3})$$

$$\alpha(T) = \left( 1 + m \left( 1 - \left( \frac{T}{T_c} \right)^{0.5} \right) \right)^2 \quad (\text{A4})$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \quad (\text{A5})$$

and the parameter  $b$  from

$$b = \frac{\Omega_b RT_c}{P_c} \quad (\text{A6})$$

$T_c$  is the critical temperature,  $P_c$  the critical pressure and  $\omega$  the acentric factor. The constants  $\Omega_a$  and  $\Omega_b$  take the values

$$\Omega_a = 0.42747 \quad \Omega_b = 0.08664 \quad (\text{A7})$$

For an  $N$ -component mixture the parameter  $a$  is in the classical formulation found from

$$a = \sum_{i=1}^N \sum_{j=1}^N z_i z_j a_{ij} \quad (\text{A8})$$

and  $b$  from

$$b = \sum_{i=1}^N z_i b_i \quad (\text{A9})$$

where  $z$  stands for mole fraction,  $i$  and  $j$  are component indices, and

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (\text{A10})$$

The parameter  $k_{ij}$  is a binary interaction coefficient.

The parameter  $c$  is the volume shift parameter. From an  $N$  component mixture it is found from

$$c = \sum_{i=1}^N z_i c_i \quad (\text{A11})$$

where  $c_i$  is the volume translation parameter of component  $i$ .

For binary pairs of components of which at least one is polar, the classical mixing rule for the  $a$ -parameter is often insufficient. Instead the mixing rule suggested by Huron and Vidal (HV) may be used. It takes the form

$$a = b \left( \sum_{i=1}^N \left( z_i \frac{a_i}{b_i} \right) - \frac{G_\infty^E}{\ln 2} \right) \quad (\text{A12})$$

where  $G_\infty^E$  is the excess Gibbs energy at infinite pressure.  $G_\infty^E$  is found using a modified NRTL mixing rule

$$\frac{G_\infty^E}{RT} = \sum_{i=1}^N z_i \frac{\sum_{j=1}^N \tau_{ji} b_j z_j \exp(-\alpha_{ji} \tau_{ji})}{\sum_{k=1}^N b_k z_k \exp(-\alpha_{ki} \tau_{ki})} \quad (\text{A13})$$

where  $\alpha_{ji}$  is a non-randomness parameter, i.e. a parameter for taking into account that the mole fraction of molecules of type  $i$  around a molecule of type  $j$  may deviate from the overall mole fraction of molecules of type  $i$  in the mixture. When  $\alpha_{ji}$  is zero, the mixture is completely random. The  $\tau$  parameter is defined by the following expression

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \quad (\text{A14})$$

where  $g_{ji}$  is an energy parameter characteristic of the  $j$ - $i$  interaction. The parameter  $b$  entering into the expression for  $G_\infty^E$  is the  $b$ -parameter of the SRK-equation. The classical mixing rule is still used for the  $b$ -parameter.

For a binary pair, which can be described using the classical mixing rule, the local composition will not deviate from the overall composition, i.e.  $\alpha_{ji}$  should be chosen equal to zero. By further selecting the following expressions for the interaction energy parameters

$$g_{ii} = -\frac{a_i}{b_i} \ln 2 \quad (\text{A15})$$

$$g_{ji} = -2 \frac{\sqrt{b_i b_j}}{b_i + b_j} (g_{ii} g_{jj})^{0.5} (1 - k_{ij}) \quad (\text{A16})$$

the H&V mixing rule reduces to the classical one. When the H&V mixing rule is used, Eqs. (A15) and (A16) are therefore used for  $g_{ij}$  and  $g_{ii}$  of binary pairs, which do not require the advanced mixing rule.

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