Peng–Robinson predictions for hydrocarbons, CO_2, N_2, and H_2S with pure water and NaCl brine

Ingolf Søreide [a] and Curtis H. Whitson

Dept. of Petroleum. Eng., UNIT-NTH, 7036 Trondheim (Norway)

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ABSTRACT

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Attempts at predicting mutual solubilities with a conventional cubic equation of state (EOS) including the effect of salts in the aqueous phase have so far been limited. The main purpose of this work is to provide a simple and novel approach for predicting mutual solubilities of brine/hydrocarbon mixtures with an EOS at high pressures and temperatures, including the effect of salinity in the aqueous phase. The Peng–Robinson EOS * has been applied in this study with two modifications: (1) an α-term in the EOS constant a has been developed specifically for the water/brine component as a function of sodium chloride (NaCl) brine salinity and pure water reduced temperature, T_r, and (2) two sets of binary interaction parameters (BIP) in the classical mixing rule for mixture EOS constant a have been determined as a function of acentric factor, temperature, and salinity. Experimental data of vapor pressures and mutual solubilities provide the basis for the proposed methods. Applications of the methods described include phase behavior prediction of reservoir gas–oil/brine systems at high pressures, including (1) gas solubility in water/brine and (2) water solubility in hydrocarbon reservoir fluids.

INTRODUCTION

Most naturally occurring petroleum reservoir fluids contain water or brine. Conventional equations of state (EOSs), e.g. the PR EOS or the

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Correspondence to: I. Søreide, Norsk Hydro a/s, P.O. Box 200, Stabekk, N-1321, Norway.
[a] Current address: see *Correspondence* address.
* Robinson and Peng, 1978.

Soave–Redlich–Kwong EOS (Soave, 1972), are not adequate for representing the special interaction of water molecules that determines phase behavior of the aqueous phase in hydrocarbon–water binary mixtures. Typically, the aqueous phase gas solubility may be predicted orders of magnitude in error, while predicted compositions of the hydrocarbon-rich phase(s) are reasonably accurate. Several modifications to cubic EOSs have been proposed to achieve a better representation of mixtures including pure water.

Peng and Robinson (1980) propose two modifications of the original PR EOS to improve phase behavior prediction of hydrocarbon mixtures including water: first, a specific temperature dependency of the EOS constant a for water, $\alpha(T_r)$, is expressed

$$\alpha^{1/2} = 1.008568 + 0.8215 \left(1 - T_r^{1/2}\right), \quad T_r < 0.72 \tag{1}$$

Equation (1) results in improved water vapor pressure predictions in the range $0.44 < T_r < 0.72$ compared with the original PR EOS α-term. Secondly, two sets of binary interaction parameters (BIPs) are proposed for hydrocarbon/water binaries, one set for the non-aqueous phase(s) and one set for the aqueous phase. There is a clear empirical advantage of using this procedure, but it may lead to a thermodynamic inconsistency using two different values of constant a (Robinson et al., 1985). Despite this inconsistency, the approach should be valid away from critical conditions, which are usually not obtained for hydrocarbon/water mixtures.

Peng and Robinson (1980) applied the modified PR EOS to several binary mixtures including water and hydrocarbons (C_1–nC_6) and non-hydrocarbons commonly found in petroleum mixtures (N_2, CO_2, H_2S). A constant BIP for the non-aqueous phase(s) and a temperature-dependent BIP for the aqueous phase were found adequate to match experimental mutual solubility data with reasonable accuracy. A review of various EOS mixing rules for aqueous solutions is given by Michel et al. (1989).

Effect of salts in the aqueous phase

Attempts at predicting mutual solubilities with an EOS including the effect of salts in the aqueous phase have so far been limited. Most of the studies concerning this problem are performed at low pressures and temperatures, or use methods that are not readily applicable to systems containing supercritical gases. The work by Harvey and Prausnitz (1989) proposes an EOS for high pressure conditions using a rather complex EOS which accounts for intermolecular forces due to ionic effects, in addition to describing conventional intermolecular forces for non-electrolytes. In this model, two BIPS included in a cubic mixing rule are obtained from

room-temperature osmotic coefficients and Seconov (Setchenow) constants. Results show that the prediction is good for systems including pure water or brine with low salt content (< 1 molal). The salting-out effect is, however, underpredicted for systems with moderate to high salt content.

The main purpose of this work is to provide a simple and novel approach for predicting mutual solubilities of brine/hydrocarbon mixtures with a cubic EOS at high pressures and temperatures, including the effect of salinity in the aqueous phase. The PR EOS has been applied in this study with two modifications: (1) an α-term in the EOS constant a has been developed specifically for the water/brine component as a function of NaCl brine salinity and pure water reduced temperature, and (2) two sets of BIPs in the classical mixing rule for mixture EOS constant a have been determined as a function of acentric factor, temperature and salinity. Experimental data on vapor pressures and mutual solubilities provide the basis for the proposed methods. Applications of the modified EOS include phase behavior prediction of reservoir gas–oil/brine systems at high pressures, including (1) gas solubility in water/brine and (2) water solubility in hydrocarbon reservoir fluids.

HYDROCARBON SOLUBILITY IN WATER/NaCl BRINE SOLUTIONS

Interstitial or connate formation water in a petroleum reservoir contains varying amounts of different salts, though mainly NaCl. The presence of salts in formation water reduces the gas solubility.

A major part of this work is aimed at predicting the effect of brine salinity on gas solubilities in aqueous brine mixtures. Since data on some gas solubility of hydrocarbons in brine do not exist, "experimental" data were generated using measured gas solubilities in distilled water and Seconow salting-out coefficients to adjust for the salinity effect on solubility. This procedure is described below:

A correction for gas solubility in a brine, S_n, compared with gas solubility in distilled water, S_w, is given by Seconow in terms of a salting-out coefficient, k_s, and salinity (molal), c_{sw}:

$$S_n/S_w = 10^{-k_s c_{sw}} \tag{2}$$

where S has units of moles/litre (molarity); k_s coefficients have been presented in the literature for various hydrocarbon/brine systems, as reviewed by Long and McDevit (1952) and Zemaitis et al. (1986).

Cramer (1984) reports k_s coefficients for a one molal methane/NaCl brine binary mixture in the temperature range 0–300°C (32–572°F). These data may be fitted using the following relation:

$$k_s = 0.1813 - 7.692 \times 10^{-4}T + 2.6614 \times 10^{-6}T^2 - 2.612 \times 10^{-9}T^3 \tag{3}$$

where T is in °F. Pawlikowski and Prausnitz (1983) suggest a linear relation for k_s in terms of (ϵ_i/k):

$$k_s = A_s + B_s(\epsilon_i/k) \tag{4}$$

where ϵ_i is the Lennard-Jones energy interaction parameter for the gas component and k is Boltzmann's constant, and A_s and B_s are temperature-dependent constants given specifically for each salt at 25°C (77°F). If we assume an analogous k_s temperature dependency for hydrocarbons other than methane, eqn. (4) can be used to obtain the shift in the salting-out coefficient for ethane, propane and n-butane, k_{si}, relative to that for methane, k_{s1}.

$$k_{si} = k_{s1} + \Delta k_{si} \qquad i = C_2, C_3, nC_4 \tag{5}$$

where Δk_{si} is expressed as

$$\Delta k_{si} = B_s[(\epsilon_i/k) - (\epsilon_1/k)] \tag{6}$$

Pawlikowski and Prausnitz report $B_s = 3.56 \times 10^{-4}$ K m^{-1} for NaCl brine. ϵ_i/k may be related to the normal boiling point of the gas, T_{bi}.

$$\epsilon_i/k = 1.25 T_{bi} \tag{7}$$

with T_{bi} in K. A general k_{si} correlation results from combining eqns. (3)–(7).

$$k_{si} = 0.13163 + 4.45 \times 10^{-4} T_{bi}$$

$$- 7.692 \times 10^{-4} T + 2.6614 \times 10^{-6} T^2 - 2.612 \times 10^{-9} T^3 \tag{8}$$

with T in °F and T_{bi} in K.

Figure 1 shows a plot of salting-out coefficients versus temperature. The continuous lines represent k_s values estimated from eqn. (8) and the symbols represent k_s values for NaCl brines reported by Cramer (1984), Morrison (1952), Morrison and Billett (1952), Long and Chierici (1961) and Standing (1974). The accuracy of k_s at high temperatures for C_2, C_3 and nC_4 is questionable, but the importance of an accurate relation for these components at high temperatures is also small.

Now that a general salting-out coefficient relation (eqn. (8)) has been developed, the hydrocarbon solubility in NaCl brine may be calculated to provide an "experimental" database of hydrocarbon solubility as a function of temperature and salinity as follows:

(1) Obtain experimental data for hydrocarbon mole fraction in pure water, x_i, at specified pressure and temperature conditions.

(2) Calculate gas–water solubility, S_w ($S_w = Nx_i/(1 - x_i)$, where N is a constant dependent on units and brine properties).
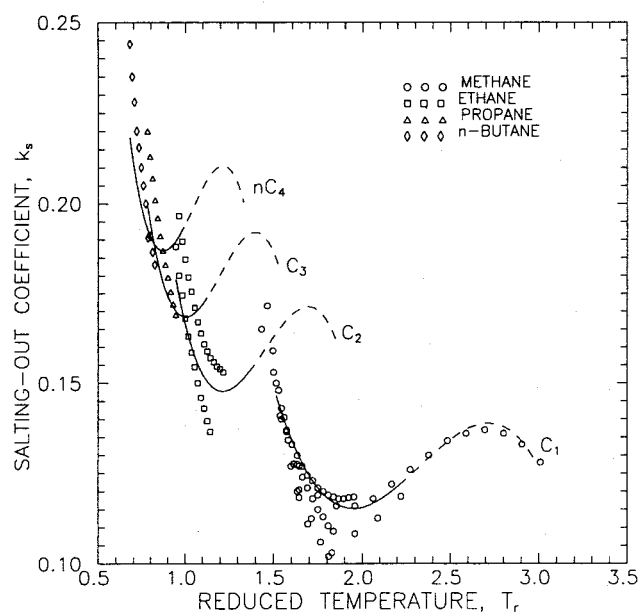
Fig. 1. Salting-out coefficients vs. hydrocarbon reduced temperature for hydrocarbon/NaCl brine mixtures: symbols represent reported coefficients from various sources, and solid lines represent eqn. (8).

(3) Calculate the ratio S_n/S_w from eqn. (2), with k_{si} estimated from eqn. (8). Gas–brine solubility, S_n, is then determined from the S_n/S_w ratio and S_w.

(4) Finally, calculate the hydrocarbon mole fraction in brine, x_{in} ($x_{in} = S_n/(N + S_n)$).

EOS MODIFICATIONS

Vapor pressure

Experimental vapor pressure data for water are given by Schmidt (1979) from 0 to 325°C [32 to 617°F], and for NaCl brine solutions of 0 to 5.0 molality from 80 to 325°C (176 to 617°F) by Haas (1976). The constant a of the PR EOS was modified for water/brine to fit these data, resulting in a relation for the α-term as a function of pure water reduced temperature, T_r, and salinity, c_{sw}:

$$\alpha^{1/2} = 1 + 0.4530\left[1 - T_r\left(1 - 0.0103c_{sw}^{1.1}\right)\right] + 0.0034\left(T_r^{-3} - 1\right) \tag{9}$$

For water the PR EOS modified with eqn. (9) predicts vapor pressure within 0.2% error from 15 to 325°C [60 to 617°F]. NaCl brine vapor

pressures may be estimated with about the same accuracy above 80°C (176°F).

Aqueous and non-aqueous phase BIPs

The EOS modification proposed by Peng and Robinson (1980) using two sets of BIPs for water–hydrocarbon solutions has been adopted in this work. For a mixture including components i and j, two different EOS constants a are determined for the non-aqueous and the aqueous phase: a_{ij}^{NA} and a_{ij}^{AQ}, respectively. These are expressed as a function of the respective phase BIPs, k_{ij}^{NA} and k_{ij}^{AQ}, and mole fractions y and x.

$$a_{ij}^{NA} = \sum_i \sum_j y_i y_j (a_i a_j)^{1/2} \left(1 - k_{ij}^{NA}\right) \tag{10a}$$

$$a_{ij}^{AQ} = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2} \left(1 - k_{ij}^{AQ}\right) \tag{10b}$$

Non-aqueous-in-aqueous phase solubilities

The sources for experimental hydrocarbon solubility data in pure water $(C_1 - nC_4/H_2O)$ used in this work are listed in Table 1. Figure 2 shows that excellent agreement with measured methane solubilities in water can be obtained with the proposed EOS modifications (eqns. (9) and (10)) at various pressures and temperatures. The k_{ij}^{AQ} values of eqn. (10) were determined by regression. The following correlation was developed:

$$k_{ij}^{AQ} = A_0 + A_1 T_{ri} + A_2 T_{ri}^2 \tag{11}$$

where i = hydrocarbon components and j = water, and the constants A_0, A_1 and A_2 are given in Table 2. The correlation may also be extrapolated to estimate k_{ij}^{AQ} for pentane and heavier components. Figure 3 compares k_{ij}^{AQ} from eqn. (11) (solid line) with the regression-based k_{ij}^{AQ} (symbols).

TABLE 1

References reporting hydrocarbon gas solubilities in pure water

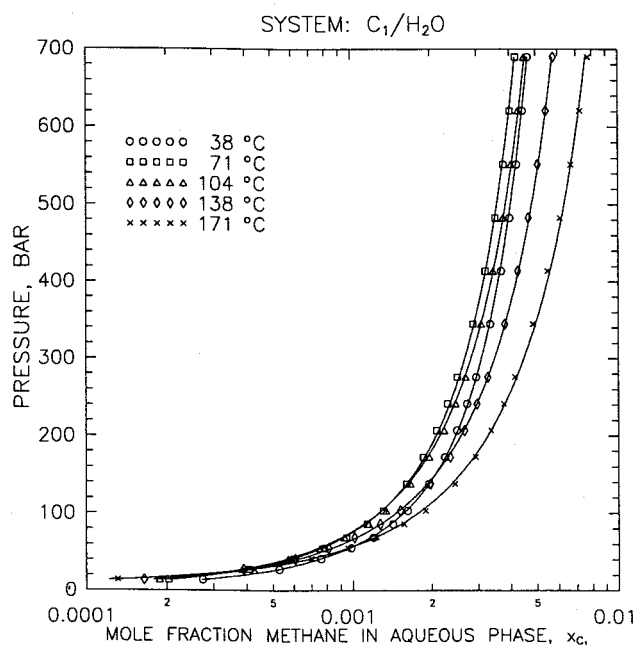| System	Reported by	p (bar)	T (°C)
C_1/H_2O	Culberson and McKetta (1951)	14–690	25–171
C_2/H_2O	Culberson and McKetta (1950)	14–690	100–171
C_3/H_2O	Kobayashi and Katz (1953)	14–207	100–154
n-C_4/H_2O	Reamer et al. (1952)	14–690	100–171

Fig. 2. Measured (symbols) and PR EOS calculated (solid lines) methane solubility in the aqueous phase at various pressures and temperatures.

Table 3 lists the physical properties used during development of eqns. (9) and (11).

Figure 4 compares generated methane solubilities (using the above procedure) in a NaCl brine of various salinities at 104°C (220°F) (symbols) with methane solubilities calculated from the modified PR EOS using best-fit k_{ij}^{AQ} values (solid lines). A k_{ij}^{AQ} correlation for hydrocarbon/NaCl brine binaries was developed from these data, and is expressed in terms of hydrocarbon T_{ri} and c_{sw}:

$$k_{ij}^{AQ} = A_0(1 + \alpha_0 c_{sw}) + A_1 T_{ri}(1 + \alpha_1 c_{sw}) + A_2 T_{ri}^2(1 + \alpha_2 c_{sw}) \tag{12}$$

The constants of eqn. (12) are listed in Table 2. Equation (12) was developed for methane, ethane, propane and n-butane in 0 to 5 molal

TABLE 2 (*Corrections to Original Publication*)
Constants in eqns. (11) and (12)

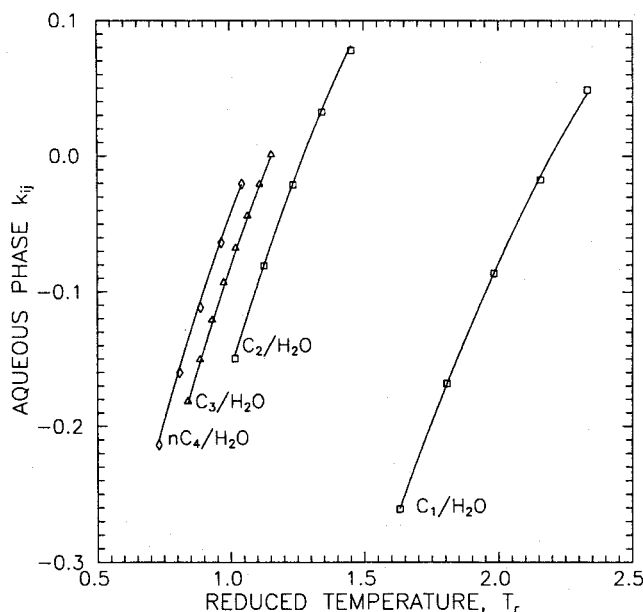|	
A_0	$1.1120 - 1.7369\omega_i^{-0.1}$
A_1	$1.1001 + 0.8360\omega_i$
A_2	$-0.15742 - 1.0988\omega_i$
α_0	**0.017407** *(corrected)*
α_1	**0.033516** *(corrected)*
α_2	**0.011478** *(corrected)*

Fig. 3. Aqueous phase interaction parameters for hydrocarbon/water binary systems as a function of hydrocarbon reduced temperature: symbols represent values determined by fitting experimental solubility data and solid lines are calculated using eqn. (11).

NaCl brine, for the pressure ranges given in Table 1, and at temperatures between 38 and 204°C (100 and 400°F). Figure 5 shows k_{ij}^{AQ} versus temperature for methane dissolved in NaCl brine of varying salinity.

TABLE 3

Physical properties of components

| Component	Mol. weight	T_c (K)	p_c (bar)	Acentric factor	T_b (K)
Carbon dioxide	44.0	304.2	73.8	0.2273	194.7
Hydrogen sulfide	34.1	373.2	89.4	0.1081	212.8
Nitrogen	28.0	126.1	34.0	0.0403	77.3
Methane	16.0	190.6	46.0	0.0108	111.6
Ethane	30.1	305.4	48.8	0.0998	184.6
Propane	44.1	369.8	42.5	0.1517	231.1
i-Butane	58.1	408.1	36.5	0.1770	261.3
n-Butane	58.1	425.2	38.0	0.1931	272.7
i-Pentane	72.2	460.4	33.8	0.2275	301.0
n-Pentane	72.2	469.6	33.7	0.2486	309.2
n-Hexane	86.2	507.4	30.1	0.3047	341.9
Water	18.0	647.3	221.2	0.3434	373.2
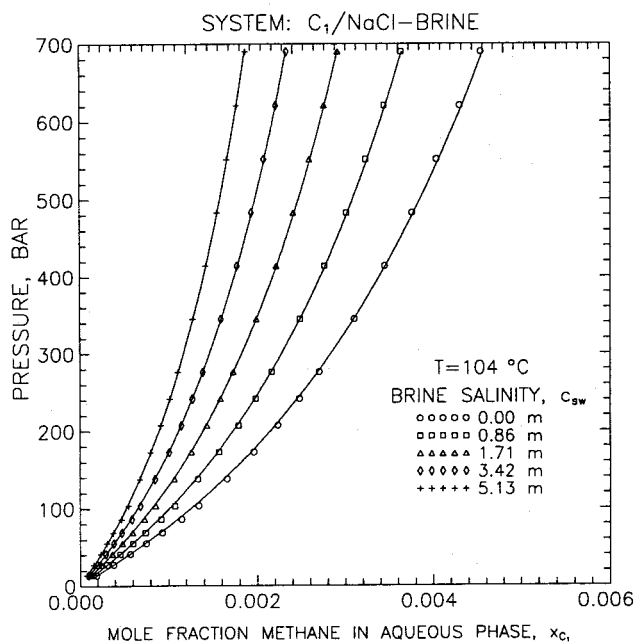
Fig. 4. Generated (symbols) and PR EOS calculated (solid lines) methane solubility in the aqueous phase at 104°C as a function of pressure and brine salinity.

The following k_{ij}^{AQ} correlations were developed for binaries including water/brine and N_2, CO_2 and H_2S, based on experimental data referred to in Table 4:
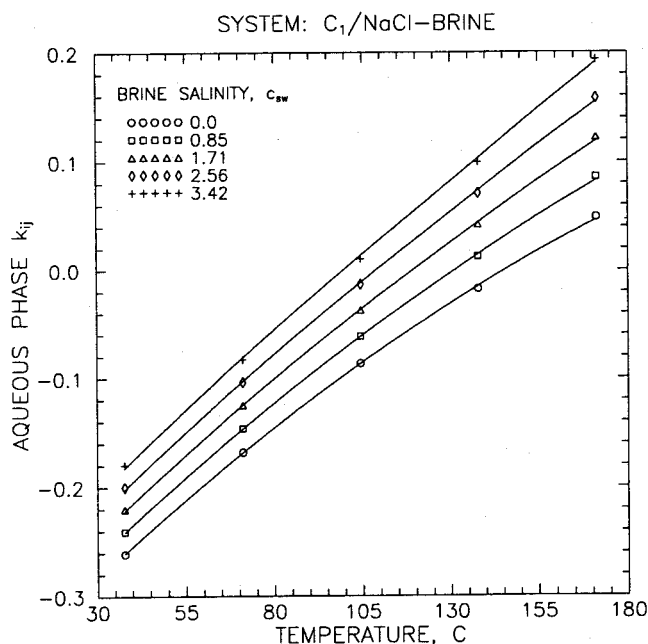

Fig. 5. Aqueous phase interaction parameters for methane/NaCl brine binary systems as a function of temperature and brine salinity: symbols represent best-fit results and solid lines represent eqn. (12).

TABLE 4

References reporting nitrogen, carbon dioxide and hydrogen sulfide solubilities in pure water and NaCl brine

System	Reported by	p (bar)	T (°C)
N_2/H_2O	Wiebe et al. (1933)	14–1035	25–100
$N_2/$brine	O'Sullivan and Smith (1970)	100– 600	52–125
CO_2/H_2O	Wiebe and Gaddy (1940, 1941)	25– 510	12– 42
CO_2/H_2O	Prutton and Savage (1945)	25– 620	38– 50
$CO_2/$brine	Takenouchi and Kennedy (1964)	14– 970	150–350
$CO_2/$brine	Yasunishi and Yoshida (1979)	1.0	15– 35
H_2S/H_2O	Selleck et al. (1952)	20– 345	38–171
H_2S/H_2O	Gillespie et al. (1984)	20– 220	71–204
H_2S/H_2O	Lee and Mather (1977)	10– 60	90–150

$N_2/$NaCl brine: (*Correction to Original Publication!!!*)

$$k_{ij}^{AQ} = -1.70235(1 + 0.025587c_{sw}^{0.75}) + 0.44338(1 + 0.08126c_{sw}^{0.75})T_{ri} \qquad (13)$$

$CO_2/$NaCl brine:

$$k_{ij}^{AQ} = -0.31092(1 + 0.15587c_{sw}^{0.7505}) + 0.23580(1 + 0.17837c_{sw}^{0.979})T_{ri}$$

$$- 21.2566 \exp(-6.7222T_{ri} - c_{sw}) \qquad (14)$$

$H_2S/$NaCl brine:

$$k_{ij}^{AQ} = -0.20441 + 0.23426T_{ri} \qquad (15)$$

where $i = N_2$, CO_2 or H_2S, and $j =$ water or brine. Figures 6 and 7 show k_{ij}^{AQ} as a function of temperature and brine salinity for $N_2/$ and $CO_2/$NaCl brine binary mixtures, respectively. Symbols represent best-fit BIPs determined for the modified PR EOS, and solid lines represent BIPs calculated from correlation eqns. (13) and (14), respectively.

The values increase linearly with increasing temperature for $N_2/$NaCl brine mixtures. For $CO_2/$NaCl brine mixtures it was observed that k_{ij}^{AQ} is a linear function of temperature above 150°C (300°F) and slightly non-linear below 150°C. Experimental data reporting solubility of CO_2 in NaCl brine for $T < 150$°C and at high pressures are not readily available. Therefore the dashed lines in Fig. 7 are not based on measured data, but rather a careful extrapolation of k_{ij}^{AQ} determined at higher temperature. It is observed that the extrapolation of $CO_2/$NaCl brine k_{ij}^{AQ} corresponds well to values obtained from solubility data reported by Yasunishi and Yoshida (1979) at atmospheric pressure (14.7 psia) in the range 15–35°C (60–95°F).

A linear relation between k_{ij}^{AQ} and $T_r(H_2S)$ was developed for the hydrogen sulfide/water binary mixture. This is illustrated in Fig. 8, which compares best-fit k_{ij}^{AQ} values obtained with the modified PR EOS and
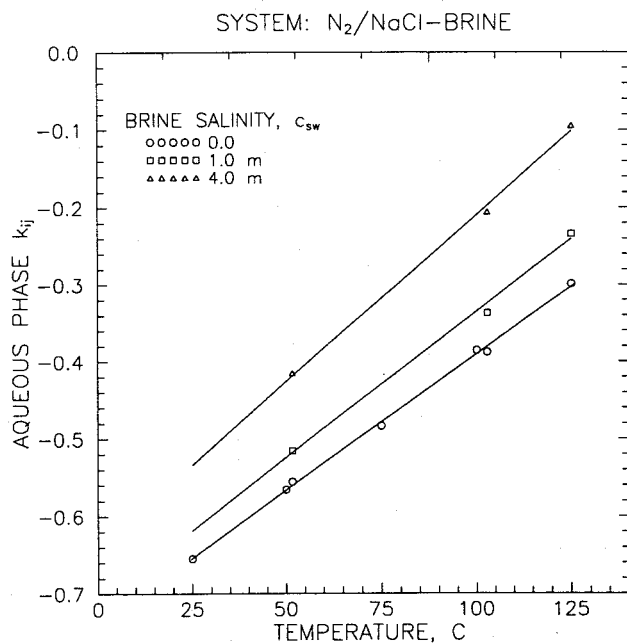
SYSTEM: N_2/NaCl−BRINE

Fig. 6. Aqueous phase interaction parameters for nitrogen/NaCl brine binary systems as a function of temperature and brine salinity: symbols represent best-fit results and solid lines represent eqn. (13).
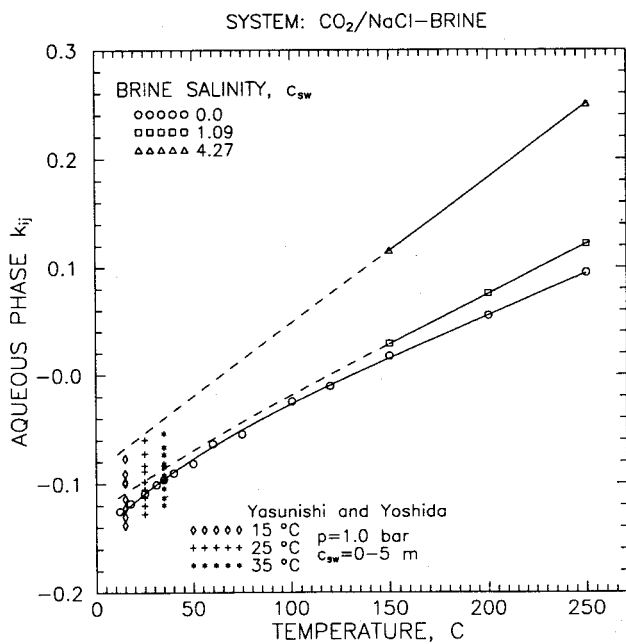
SYSTEM: CO_2/NaCl−BRINE

Fig. 7. Aqueous phase interaction parameters for carbon dioxide/NaCl brine binary systems as a function of temperature and brine salinity: symbols represent best-fit results and solid lines represent eqn. (14).
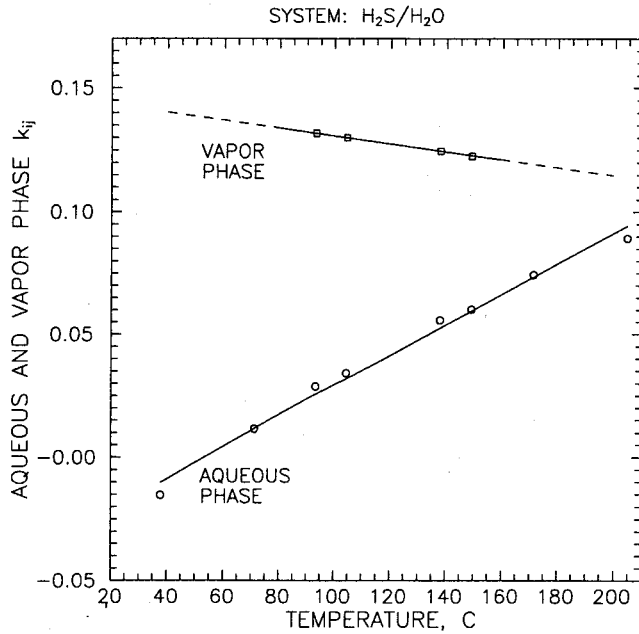
SYSTEM: H_2S/H_2O

Fig. 8. Aqueous and non-aqueous phase(s) interaction parameters for hydrogen sulfide/water binary systems as a function of temperature: symbols represent best-fit results and solid lines represent eqns. (15) and (17) for k_{ij}^{AQ} and k_{ij}^{NA}, respectively.

k_{ij}^{AQ} values from eqn. (15). Figure 9 compares experimental hydrogen sulfide gas solubilities with calculated values using the modified PR EOS and eqn. (15). The agreement is acceptable at low pressures.
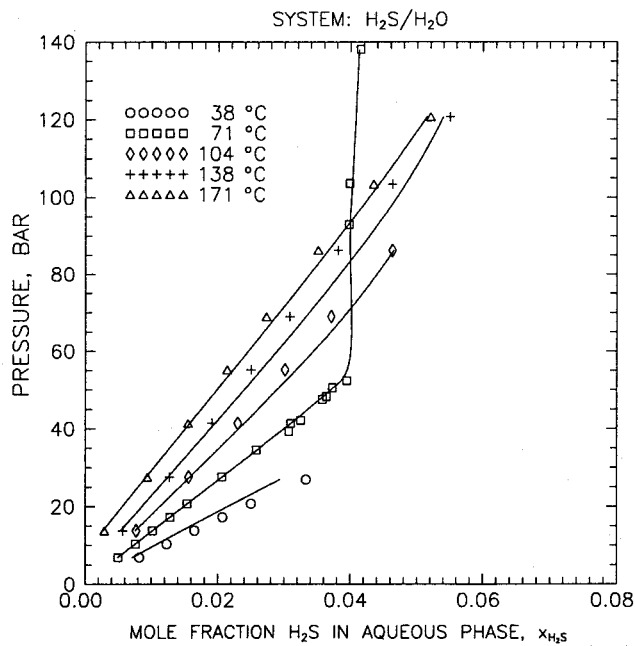
SYSTEM: H_2S/H_2O

Fig. 9. Measured (symbols) and PR EOS calculated (solid lines) hydrogen sulfide solubility in the aqueous phase at various pressures and temperature.

TABLE 5

Non-aqueous phase interaction parameters, k_{ij}^{NA}, for binary mixtures of water and various light components

Component	k_{ij}^{NA}
C_1	0.4850
C_2	0.4920
C_3	0.5525
$n\text{-}C_4$	0.5091
N_2	0.4778
CO_2	0.1896
H_2S	Eqn. 17

Aqueous-in-non-aqueous phase solubilities

Experimental water solubility data in the non-aqueous phase for mixtures containing brine have not been available in the literature. Until such data become available it is recommended that the effect of salinity be modeled using the water/brine $\alpha(c_{sw})$-term (eqn. (9)) in the PR EOS and a non-aqueous phase BIP value, k_{ij}^{NA}, independent of salinity. k_{ij}^{NA} is basically independent of temperature, i.e. a constant k_{ij}^{NA} value results in water solubilities that are in good agreement with experimental data over the entire temperature range. k_{ij}^{NA} values are presented in Table 5. These are determined on the basis of pure water solubility data reported in references listed in Table 6.

Figure 10 shows predicted water solubilities in the non-aqueous phase for a methane/NaCl brine mixture with varying brine salinity. The predicted reduction in water solubility for mixtures containing brine, relative

TABLE 6

References reporting non-aqueous phase(s) water solubility for some hydrocarbon/ and non-hydrocarbon/water systems

| System	Reported by	p (bar)	T (°C)
C_1/H_2O	Olds et al. (1942)	14–670	38–238
C_2/H_2O	Reamer et al. (1943)	14–670	38–238
C_3/H_2O	Kobayashi and Katz	14–207	38–154
$n\text{-}C_4/H_2O$	Reamer et al. (1952)	14–670	38–238
N_2/H_2O	Peng and Robinson (1985)	7–103	25–100
CO_2/H_2O	Takenouchi and Kennedy (1964)	14–966	150–350
H_2S/H_2O	Selleck et al. (1952)	14–345	38–171
H_2S/H_2O	Gillespie et al. (1984)	20–220	71–204
H_2S/H_2O	Lee and Mather (1977)	10–40	71
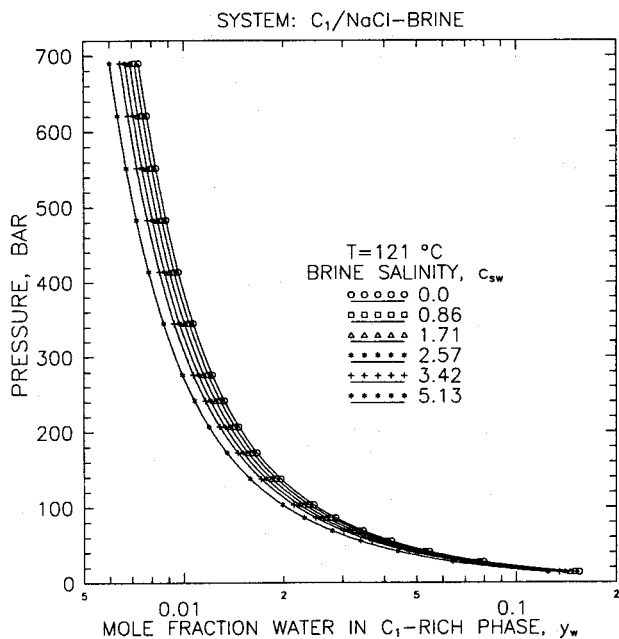
Fig. 10. Measured (symbols) and PR EOS calculated (solid lines) water solubility in the non-aqueous phase of a methane/NaCl brine system at 121°C as a function of pressure and brine salinity.

to solubility for mixtures containing pure water, is for practical purposes independent of pressure and temperature. The ratio y_w/y_w^0 calculated by the modified PR EOS is correlated against salinity in Fig. 11. The effect of
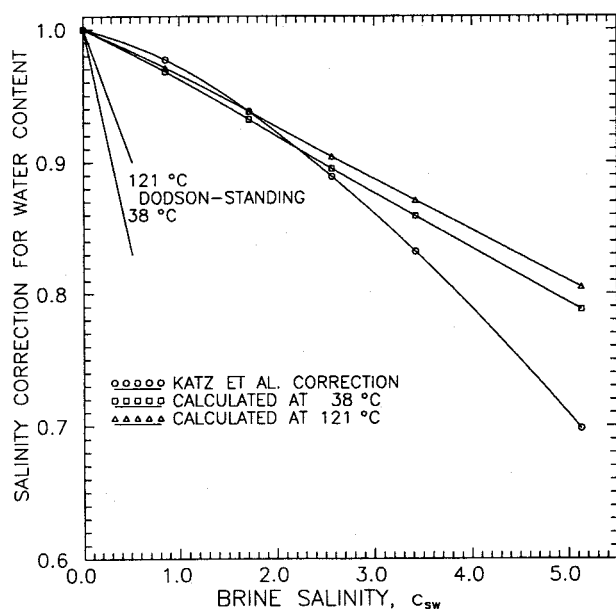

Fig. 11. Effect of brine salinity on water solubility in the non-aqueous vapor phase for a methane/NaCl brine mixture: "calculated" refers to use of the PR EOS modified with eqns. (9) and (10).
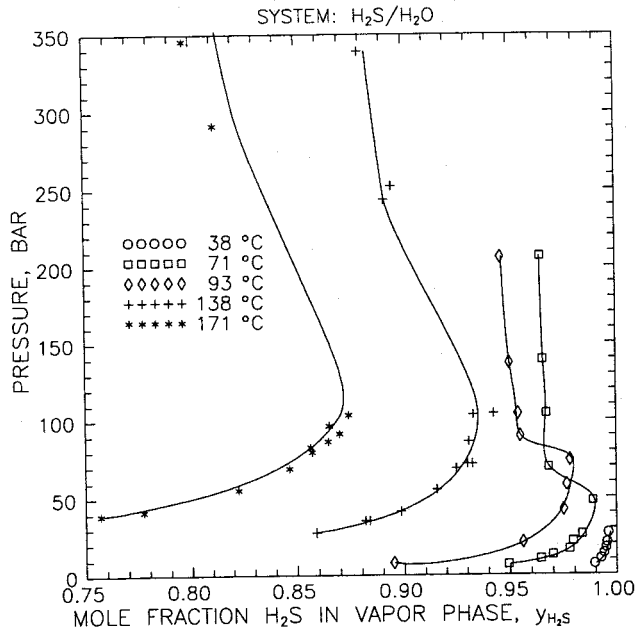
Fig. 12. Measured (symbols) and PR EOS calculated (solid lines) water solubility in the hydrogen sulfide-rich vapor phase.

salinity is clearly less than that reported by Dodson and Standing (1944) in the salinity range 0.0 to 0.6 molal, and is consistent with the correlation of Katz et al. (1959) up to a molality of about 3.0. The Katz y_w/y_w^0-relation can be expressed in terms of c_{sw} as

$$\frac{y_w(\text{brine})}{y_w^0(\text{water})} \approx \frac{p_w(\text{brine})}{p_w^0(\text{water})} = 1 - 0.02865 c_{sw}^{1.44} \tag{16}$$

where p_w and y_w represent vapor pressure and vapor phase mole fraction, respectively.

For the H_2S/H_2O system k_{ij}^{NA} is slightly dependent on temperature as shown in Fig. 8, resulting in the following relation:

$$k_{ij}^{NA} = 0.19031 - 0.05965 T_{ri} \qquad i = H_2S \tag{17}$$

Figure 12 shows that calculated water solubilities in the H_2S-rich vapor phase compares well with experimental data, especially at pressures below 100 bar (1500 psi).

APPLICATIONS

In this section the proposed methods are applied to compare predicted mutual solubilities with measured data. Figure 13 compares predicted
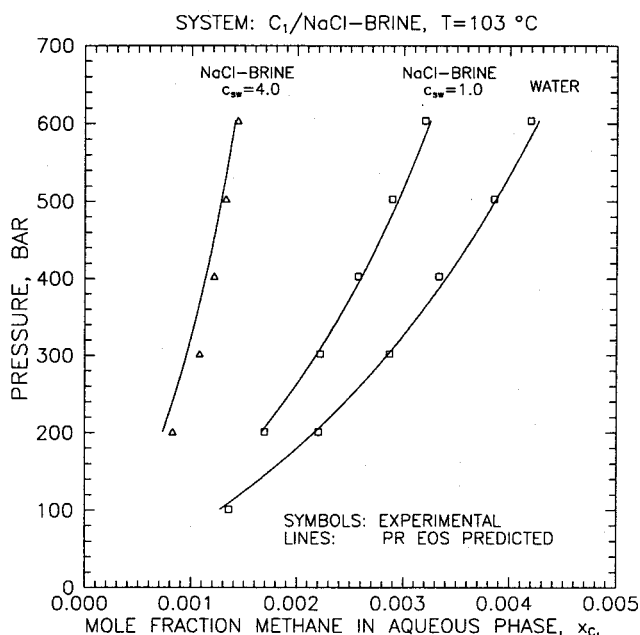
Fig. 13. Measured (symbols) and predicted (solid lines) methane solubility in the aqueous phase of a methane/NaCl brine system at 103°C as a function of pressure and brine salinity (experimental data from O'Sullivan and Smith, 1970).

methane solubilities in NaCl brine at 103°C with measured data reported by O'Sullivan and Smith (1970). Brine salinity ranges from 0.0 to 4.0 m, at pressures from 100 to 600 bar. It is observed that the PR EOS, modified with eqns. (9), (10) and (12), reproduces the experimental data accurately. Similar data are reported by Price et al. (1982) for C_1/NaCl brine with salinity varying from 0.0 to 5.1 m, and pressures from 250 to 1550 bar. The comparison between predicted and measured data presented in Fig. 14 shows that C_1 solubility is slightly underestimated at 170°C at $c_{sw} = 0.0$, 1.9 and 5.1 m. The comparison shows that the deviations are most pronounced at high pressures (> 1000 bar).

O'Sullivan and Smith also reported N_2 solubility in NaCl brine under similar conditions. A comparison of measured and predicted data is shown in Fig. 15. Again the modified PR EOS performs very well, except at $c_{sw} = 1.0$ m where N_2 solubility is somewhat underpredicted. The aqueous phase liquid composition for a CO_2/NaCl brine mixture is presented by Takenouchi and Kennedy (1965) at 150°C at pressures from 100 to 1400 bar. Figure 16 compares calculated and measured solubility data in the pressure range from 100 to 400 bar.

Dodson and Standing (1944) reported measured solubilities of natural gas in pure water and in two oil-field brines. The pressure and temperature ranges in this study were 34.5–345 bar and 37.7–121°C. The salinity of the
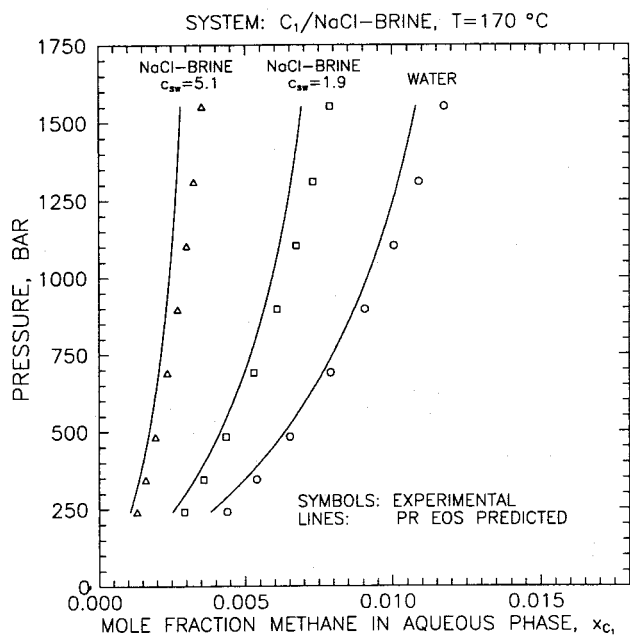
Fig. 14. Measured (symbols) and predicted (solid lines) methane solubility in the aqueous phase of a methane/NaCl brine system at 170°C as a function of pressure and brine salinity (experimental data from Price et al., 1982).
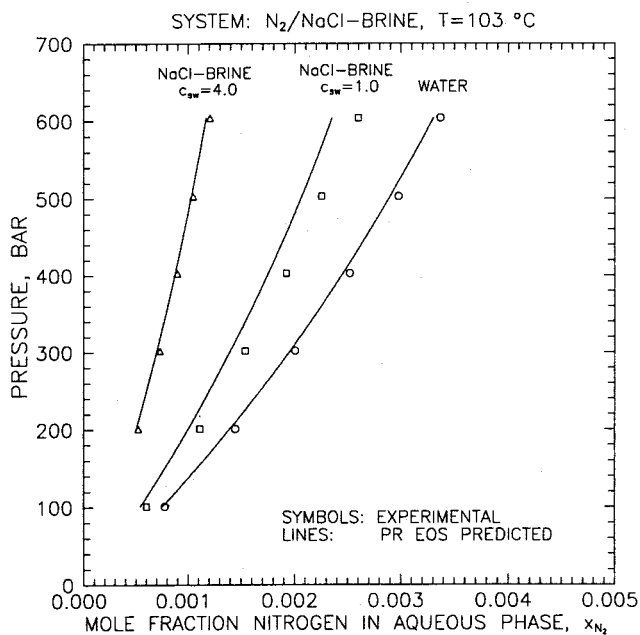

Fig. 15. Measured (symbols) and predicted (solid lines) nitrogen solubility in the aqueous phase of a nitrogen/NaCl brine system at 103°C as a function of pressure and brine salinity (experimental data from O'Sullivan and Smith, 1970).
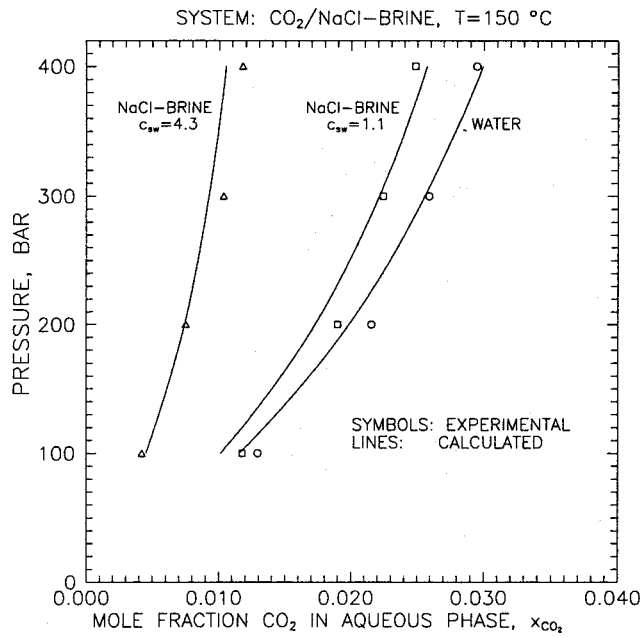
SYSTEM: CO_2/NaCl–BRINE, T=150 °C

Fig. 16. Measured (symbols) and predicted (solid lines) carbon dioxide solubility in the aqueous phase of a carbon dioxide/NaCl brine system at 150°C as a function of pressure and brine salinity (experimental data from Takenouchi and Kennedy, 1964).

two brines denoted "Brine A" and "Brine B" were 8630 ppm ($c_{sw} \approx 0.15$ m) and 341000 ppm ($c_{sw} \approx 0.60$ m), respectively. Although different types of salt were included in Brine A and Brine B, they were treated as NaCl

Fig. 17. Measured (symbols) and predicted (solid lines) natural gas solubility in the aqueous phase for the systems natural gas/water and natural gas/"Brine B" at 37.8°C (experimental data from Dodson and Standing, 1944).
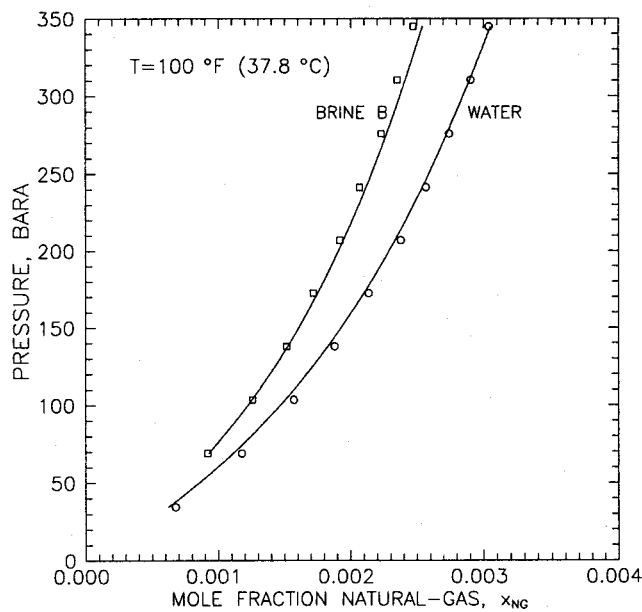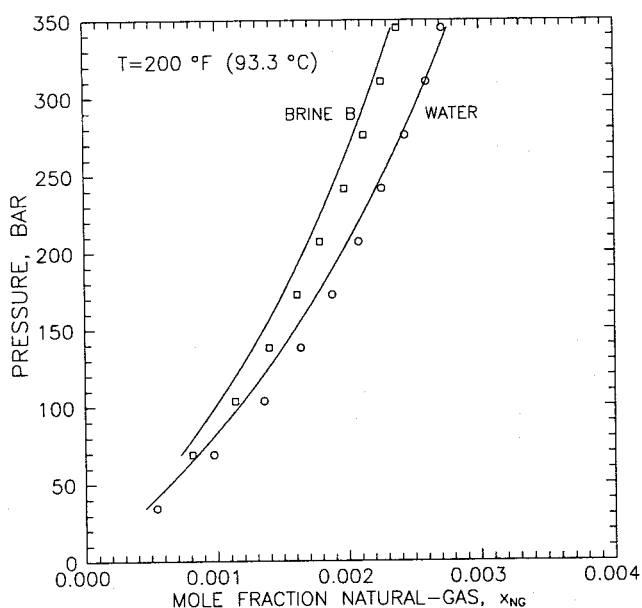
Fig. 18. Measured (symbols) and predicted (solid lines) natural gas solubility in the aqueous phase for the systems natural gas/water and natural gas/"Brine B" at 93.3°C (experimental data from Dodson and Standing, 1944).

brines. The natural gas used by Dodson and Standing contained 88.5 mol% C_1 and less than 1 mol% C_{5+}; the average molecular weight of the gas was 19.
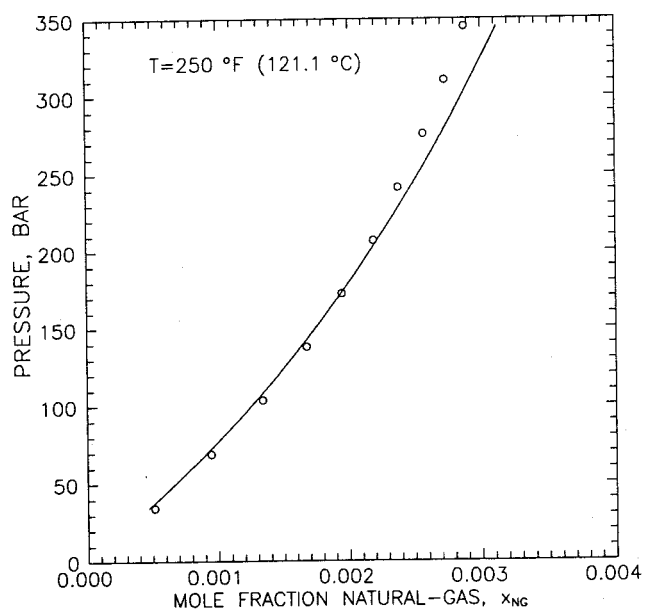

Fig. 19. Measured (symbols) and predicted (solid lines) natural gas solubility in the aqueous phase for the system natural gas/water at 121.1°C (experimental data from Dodson and Standing, 1944).
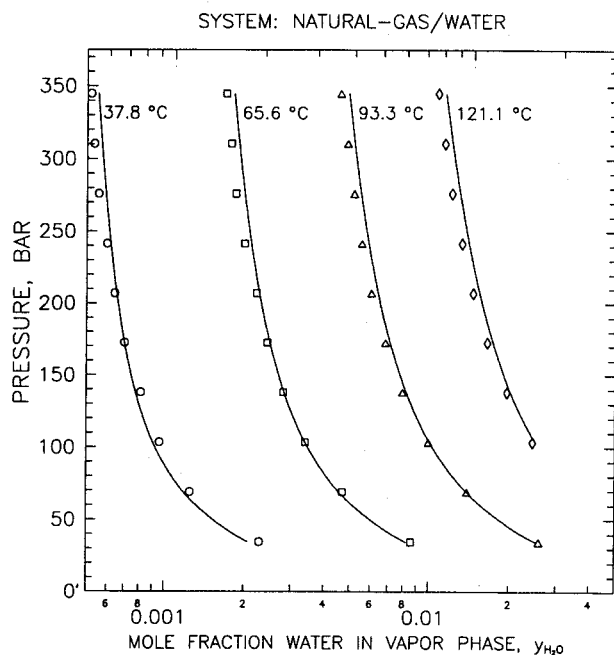
Fig. 20. Measured (symbols) and PR EOS predicted (solid lines) water solubility in the hydrocarbon-rich vapor phase of a natural gas/water system at various temperatures (experimental data from Dodson and Standing, 1944).

To check performance of the proposed methods using the modified PR EOS for multicomponent mixtures, predicted natural gas solubilities were compared with the data of Dodson and Standing. These comparisons are presented in Figs. 17, 18, and 19 for 38, 94 and 121°C, respectively. It is shown that the predicted natural gas mole fraction in distilled water and in "Brine B" is very accurate, except for slight deviations at pressures above 250 bar at 121°C.

Dodson and Standing also reported water solubility in the natural gas. Figure 20 shows that the prediction of these data is quite good when using the modified PR EOS and the k_{ij}^{NA}'s listed in Table 5. A k_{ij}^{NA} value equal to 0.5 has been used for hydrocarbon/water binaries not listed in Table 5. For all hydrocarbon/brine binaries eqn. (12) was applied to calculate k_{ij}^{AQ}.

CONCLUSIONS

Mutual solubilities have been accurately predicted with a modified PR EOS for hydrocarbon/NaCl brine and some non-hydrocarbon/NaCl brine mixtures. The modifications consist of:

(1) Using a modified α-term in the EOS constant a for the brine component as a function of water reduced temperature and brine salinity.

(2) Using two sets of BIPs for each binary including water/brine k_{ij}^{AQ} and k_{ij}^{NA} for the aqueous phase and non-aqueous phase, respectively. k_{ij}^{AQ} is expressed as a function of NaCl brine salinity, hydrocarbon acentric factor and reduced temperature. Specific k_{ij}^{NA} correlations have also been developed for $N_2/$, $CO_2/$ and $H_2S/NaCl$ brine mixtures. For k_{ij}^{NA} a constant value is applied, except for $k_{ij}^{NA}(H_2S)$.

The proposed methods have been demonstrated by comparing predicted and measured solubility of C_1, N_2, and CO_2 in NaCl brine of varying salinity. Acceptable accuracy has been obtained over a wide range of pressure and temperature conditions.

Natural gas solubility in water and in two oil-field brines of varying salinity has been predicted with good agreement with measured data over a wide range of pressures and temperatures. Also, the predicted water solubility in natural gas agrees well with measured data.

ACKNOWLEDGMENT

LIST OF SYMBOLS

a, b	EOS constants
a_0, a_1, a_2, a_3	constants of salting-out coefficient correlation
A_i	constants of eqns. (11) and (12)
A_s, B_s	constants of salting-out coefficient correlation
C_{sw}	brine salinity $10^6 \, (m_s/m_s + m_w)$ (ppm)
c_{sw}	brine salinity $10^3 \, n_s/m_w$ (molality)
k	Boltzmann's constant
k_{ij}^{AQ}	aqueous phase interaction parameter for binary i, j
k_{ij}^{NA}	non-aqueous phases interaction parameter for binary i, j
k_s	salting-out coefficient, molality^{-1}, m^{-1}
M_s	molecular weight of salt ($M_s = 58.44$ for NaCl)
p	pressure (bar [psi])
p_c	critical pressure (bar [psi])
S_n	solution gas–brine ratio (mol^{-1}) (molarity)
S_w	solution gas–water ratio (mol^{-1}) (molarity)
T	temperature (°C [°F])
T_b	normal boiling point temperature (K [°R])
T_c	critical temperature (K [°R])

T_r	reduced temperature $(T_r = T/T_c)$
x_i	normalized mole fraction of aqueous phase
y_i	normalized mole fraction of non-aqueous phase

Greek letters

α	temperature-dependent parameter in EOS constant a
α_i	constants of eqn. (12)
Δk_{si}	shift in salting-out coefficient, m^{-1}
ϵ	Lennard-Jones energy interaction parameter
ω_i	acentric factor

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Errata to:

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Ingolf Søreide, Norsk Hydro

Curtis H. Whitson, PERA a/s, P.O. Box 1977 Moholt, 7448 Trondheim, Norway.

N_2/NaCl brine: (*Correction to Original Publication*)

$$k_{ij}^{AQ} = -1.70235(1 + \mathbf{0.025587}c_{sw}^{0.75}) + 0.44338(1 + 0.08126c_{sw}^{0.75})T_{ri} \qquad (13)$$

TABLE 2 (*Corrections to Original Publication*)
Constants in eqns. (11) and (12)

A_0	$1.1120-1.7369\omega_i^{-0.1}$
A_1	$1.1001+0.8360\omega_i$
A_2	$-0.15742-1.0988\omega_i$
α_0	**0.017407** *(corrected)*
α_1	**0.033516** *(corrected)*
α_2	**0.011478** *(corrected)*

Aqueous Phase BIPs $k_{ij\,AQ}$
(for hydrocarbons)