

Calculation of CO₂, CH₄ and H₂S Solubilities in Aqueous Electrolyte Solution at High Pressure and High Temperature

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This paper reports an investigation into the characterisation of liquid–vapor electrolyte solutions at high pressure and high temperature. A procedure to enable calculations of methane, carbon dioxide and hydrogen sulphide solubilities in brines (0–6 m.) for temperature from 25 to 350°C and for pressures from 1 to 1800 bar is presented. The model is based on Helgeson, Kirkham and Flowers modified equations of state (HKF) and on the semi–empirical interaction model introduced by Pitzer. HKF modified equations of state are used to calculate the reference fugacity of gas species, and the Pitzer ionic interaction model is used to calculate the activity coefficient of dissolved species (i.e. ionic or neutral).

The efficiency of the combination of the two models is confirmed by several comparisons with data in the literature.

Keywords: vapor–liquid equilibria, solubility, electrolytes solutions, high temperature, high pressure.

INTRODUCTION

Phase behaviour in aqueous electrolyte systems is of interest for numerous industrial applications such as scale formation prediction, hydrometallurgy, distillation, gas storage, water pollution control. Because of economical, technical and ecological considerations, accurate prediction of gas solubilities in electrolyte solutions over a wide range of temperatures, pressures, and ionic strength is needed.

During migration, production, transport and stocking, petroleum fluids are in contact with salted water (i.e. formation water, sea water or injection water). Equilibria between aqueous and gas phases are affected by the presence of salts as shown by numerous experimental results^[1,2]. Gas solubility can be increased «salting in» or decreased «salting out» by the presence of one or several salts in the solution.

Therefore, during underground storage of gas with an aquifer layer it is important to forecast the potential loss of different components according to their solubility in salted water.

Industries must control the concentrations of undesirable compounds such as acid gas before industrial fluids are released into the environment. CO₂ and H₂S are often encountered in natural and industrial systems. Effective tools are needed for a good description of the physical and chemical properties of electrolyte solutions in order to recover H₂S and CO₂ from the process plant stream.

Continuing earlier work on the characterisation of electrolyte solutions^[3], this publication reports on CH₄, CO₂ and H₂S solubilities in brines (0–6 m). We combined two thermodynamic models which were developed separately. Modified Helgeson, Kirkham and Flowers (HKF) equations of state (Tanger and Helgeson^[4], Shock et al.^[5]) are used to calculate the reference fugacity of neutral species. The combination

Received March, 1997.

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List of Symbols		Greek Symbols	
$a_1, a_2, a_3, a_4, c_1, c_2$	HKF equations of state parameters	θ	solvent parameter (228 K)
f	fugacity	ϵ	dielectric constant of H ₂ O
G^{ex}	excess Gibbs energy	γ	activity coefficient
H	henry constant	λ	binary interaction parameter
l	ionic strength	μ	ternary interaction parameter
j	solvent function	Ψ	solvent parameter (2600 bar)
K	equilibrium constant	$\beta_{Ma}^{(0)}$	numerical binary interaction parameter
m	molality (mole per kilogram of water)	Subscripts	
P	pressure (bar)	i	component i
r	electrostatic radius	g	gaseous species
R	gas constant	r	reference temperature or pressure
T	temperature (K)	Superscripts	
w	conventional Born coefficient	l	liquid phase
y_i	vapor mole fraction of component i	v	vapor phase
Y	Born function	$^\circ$	standard state
z_i	ionic charge of component i		

of these equations with the Pitzer ionic interaction model allows better characterisation of thermodynamic equilibrium for complex electrolyte systems in over wide range of pressure, temperature and concentration.

The Pitzer model^[6] was developed to describe the thermodynamic properties of aqueous solutions of electrolytes. Since 1973, numerous papers have been published in which ion-interaction equations are used to accurately characterise electrolyte solutions. Moller^[7], Greenberg and Moller^[8] applied the Pitzer model to predict mineral solubilities for temperatures up to 250°C. Pitzer's specific equation has been applied by several authors to calculate gas solubilities in high temperature, high pressure concentrate brines^[9,10,11].

Modified HKF equations of state (Tanger and Helgeson^[4]) have been successfully applied to calculate the thermodynamics and transport properties of aqueous species at high pressures and temperatures. These equations can be used for ionic species^[12], inorganic neutral species^[13] and organic species^[14] for temperature up to 1000°C and pressure up to 5000 bar. Lelkers et al.^[15] have recently published a summary of the apparent standard molal Gibbs free energies of formation for 348 species including both inorganic and organic aqueous ions, neutral species and metal ligand complex, calculated using HKF modified equations.

Basic equations of both model and thermodynamic relations used to perform VLE are presented. Pitzer model binary interaction parameters for H₂S-NaCl were fitted to experimental data. CH₄, CO₂ and H₂S

solubilities calculated with this procedure are discussed and compared with literature data.

MODIFIED HKF EQUATIONS OF STATE

Algorithms have been developed in 1981 to calculate thermodynamic and transport properties of aqueous species at high pressures and temperatures^[16], then proposed in a revised version^[4,5] standard partial molar volume, heat capacity, entropy, enthalpy and Gibbs free energy of formation of 348 species including both inorganic and organic aqueous ions and neutral species can be calculated at pressures up to 5000 bar and temperatures up to 1000°C using the modified HKF equations of state^[15].

The standard partial molal Gibbs free energy for minerals or gases is given by:

$$\begin{aligned}
 \Delta \bar{G}^0 = & \Delta \bar{G}_r^0 - \bar{S}_{P_r, T_r}^0 (T - T_r) \\
 & - c_1 \left(T \ln \left(\frac{T}{T_r} \right) - T + T_r \right) \\
 & + a_1 (P - P_r) + a_2 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \\
 & - c_2 \left(\left(\left(\frac{1}{T - \theta} \right) - \left(\frac{1}{T_r - \theta} \right) \right) \left(\frac{\theta - T}{\theta} \right) \right. \\
 & \left. - \frac{T}{\theta_2} \ln \left(\frac{T_r (T - \theta)}{T (T_r - \theta)} \right) \right) \\
 & + \left(\frac{1}{T - \theta} \right) \left((a_3 (P - P_r)) + a_4 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \right) \\
 & + w \left(\frac{1}{\epsilon} - 1 \right) - w_{P_r, T_r} \left(\frac{1}{\epsilon_{P_r, T_r}} - 1 \right) \\
 & + w_{P_r, T_r} Y_{P_r, T_r} (T - T_r)
 \end{aligned} \quad (1)$$

where $\Delta\bar{G}_f^0$ is the Gibbs free energy of formation of the species from the element at a reference pressure P_r (1 bar) and reference temperature T_r (298.15 K); \bar{S}_{P_r, T_r}^0 is the standard partial molal entropy of the species at the reference pressure and temperature, a_1, a_2, a_3, a_4, c_1 and c_2 refer to temperature and pressure independent parameters characteristic of the aqueous species; \square and $*$ represent solvent parameters equal to 228 K and 2600 bar, respectively; ε and ε_{P_r, T_r} designate the dielectric constant of H₂O at the temperature and pressure of interest and T_r, P_r respectively. Y_{P_r, T_r} is given by:

$$Y_{P_r, T_r} = \frac{1}{\varepsilon_{P_r, T_r}^2} \left(\frac{\partial \varepsilon}{\partial T} \right)_{P_r, T_r} \quad (2)$$

w represents the conventional Born coefficient of the species, which can be expressed as:

$$w = \eta(Z^2(r_{e, P_r, T_r} + |Z|j)^{-1} - Z(3.082 + j)^{-1}) \quad (3)$$

where j designates a solvent function of temperature and density^[5], $\eta = 1.66027 \times 10^5 \text{ \AA cal mol}^{-1}$, Z is the charge of the species and r_{e, P_r, T_r} refers to the effective electrostatic radius of the species at the reference pressure and temperature. Detailed expressions are given by Shock et al.^[5].

In the case of neutral aqueous species, effective Born coefficients w are obtained by regression of experimental data and taken to be independent of temperature and pressure. It follows that Eq.(1) reduces to:

$$\begin{aligned} \Delta\bar{G}^0 &= \Delta\bar{G}_f^0 - \bar{S}_{P_r, T_r}^0(T - T_r) \\ &- c_1 \left(T \ln \left(\frac{T}{T_r} \right) - T + T_r \right) \\ &+ a_1(P - P_r) + a_2 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \\ &- c_2 \left(\left(\left(\frac{1}{T - \theta} \right) - \left(\frac{1}{T_r - \theta} \right) \right) \left(\frac{\theta - T}{\theta} \right) \right. \\ &\left. - \frac{T}{\theta^2} \ln \left(\frac{T_r(T - \theta)}{T(T_r - \theta)} \right) \right) + \left(\frac{1}{T - \theta} \right) \\ &\times \left(a_3(P - P_r) + a_4 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \right) \\ &+ w \left(Y_{P_r, T_r}(T - T_r) \right) \\ &+ \left(\frac{1}{\varepsilon_{P_r, T_r}} - 1 \right) - \left(\frac{1}{\varepsilon} - 1 \right) \end{aligned} \quad (2)$$

Equilibrium constant K can be calculated from the definition of the standard partial molal Gibbs free energy of reaction $\Delta\bar{G}_r^0$ given by:

$$\ln K_r = \frac{-\Delta\bar{G}_r^0 - r}{RT} \quad (4)$$

with,

$$\Delta\bar{G}_r^0 = \sum_i \nu_{i,r} \Delta\bar{G}_i^0 \quad (5)$$

where $\nu_{i,r}$ is the reaction coefficient of the i^{th} species in the reaction r and R the gas constant (8.314 J.K.⁻¹mol⁻¹).

If we consider the equilibrium between an aqueous and vapor constituent:

$$A_{(aq)} = A_{(v)} \quad (6)$$

following Shock et al.^[14], the dissociation constant K_r of the above reaction is related to fugacity and activity of the neutral solute according to:

$$K_r = \frac{f_n^v}{a_n} \quad (7)$$

since activity and reference fugacity are correlated by:

$$a_n = \frac{f_n^l}{f_n^0} \quad (8)$$

where f_n^0 stands for the standard state fugacity of species n . Eqs.(7) and (8) yield to the following equality:

$$K_r = f_n^0 \quad (9)$$

PITZER MODEL

Pitzer^[6] developed a formalism that describes the thermodynamics of electrolytes up to high concentrations, pressure and temperatures. Numerous articles give complete details of the Pitzer equations^[17]; therefore we recall only the features essential for understanding the proposed procedure.

The fundamental equation of the interaction model is a Virial expansion of the excess Gibbs energy of an electrolyte solution:

$$\begin{aligned} \frac{G^{ex}}{n_w RT} &= f(l) + \sum_i \sum_j \lambda_{ij}(l) m_i m_j \\ &+ \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k \end{aligned} \quad (10)$$

The function $f(l)$ is a modified Debye-Hückel term, where $l = \frac{1}{2} \sum_i m_i z_i^2$ is the ionic strength, m_i the molality of component i (mole per kilogram of H_2O), $\lambda_{i,j}$ the ionic strength-dependent second virial coefficient and $\mu_{i,j,k}$ related to ternary interactions. Appropriate derivatives of the above expression yield to activity coefficient of dissolved species, i.e. ions and neutral.

The activity coefficient of a dissolved neutral species (gas) as given by Pitzer's equation is:

$$\ln \gamma_N = 2 \sum_n \lambda_{Nn} m_n + 2 \sum_c \lambda_{Nc} m_c + 2 \sum_a \lambda_{Na} m_a + \sum_c \sum_a m_a m_c \Gamma_{a,c,N} \quad (11)$$

where, n, c and a refer respectively to neutral species, cations and anions.

For an aqueous system containing a non-dissociating gas, with a molality m_g , and a completely dissociated salt, given m_a anion and m_c cation and considering that at the concentration discussed in this article we can neglect the dissociation of CO_2 and H_2S in the liquid phase and the molecule-molecule interaction, equation (11) can be rewritten as:

$$\ln \gamma_g = 2\beta_{g,a}^{(0)} m_a + 2\beta_{g,c}^{(0)} m_c + m_a m_c \gamma_{g,a,c} \quad (12)$$

where $\beta^{(0)}$ stands for gas-ion binary interaction parameter.

Electrical neutrality of the solution requires that all ion-neutral parameter involving one particular ion should be set to zero. In our study we set to zero the parameter involving Cl^- .

GAS SOLUBILITIES: THERMODYNAMIC RELATIONS

In an aqueous two-phase (liquid and vapor) system at constant temperature T and pressure P , equilibrium equation of any species partitioning between the phases can be expressed in terms of fugacities:

$$f_g^l = f_g^v \quad (13)$$

where l and v designate respectively the liquid and vapor phase.

The liquid phase fugacity of component i in a mixture with respect to its value at the reference standard state, denoted by $^\circ$, can be written as:

$$f_g^l = m_g \gamma_g f_g^\circ \quad (14)$$

where γ_g is the activity coefficient on the molal scale, f_g° is the fugacity of gas in the standard state and m_g is the gas concentration in the liquid.

We can rewrite Eq.(13) as:

$$f_g^v = m_g \gamma_g f_g^\circ \quad (15)$$

Vapor phase fugacity is calculated using the Peng-Robinson cubic equation of state^[18]. HKF equations of state are used to calculate the standard state fugacity f_g° . The Pitzer semi-empirical model is used to calculate γ_g .

CALCULATED CO_2 AND CH_4 SOLUBILITIES IN $NaCl$ AND Na_2SO_4 SOLUTIONS

The solubilities of carbon dioxide and methane in sodium chloride and sodium sulfate solutions have been calculated by numerical fit of the above expression (Eq.15).

For the HKF equation of state's parameters, all the data are from references^[13,14]. For the Pitzer model, binary and ternary parameters values are from Rumpf and Maurer^[19] for $CO_2-H_2O-Na_2SO_4$, from Rumpf et al.^[11] for the system $CO_2-H_2O-NaCl$ and from Duan et al.^[20] for the $CH_4-H_2O-NaCl$ system.

Predicted CO_2 solubility values are plotted versus $NaCl$ concentration. Figs.1,2 and 3 compare calculated values and experimental data from references^[1,21]. Figs.4 through 6 illustrate our results for the system $CO_2-H_2O-Na_2SO_4$; experimental values are taken from reference^[19]. Calculated methane solubilities are compared with those reported by Duan et al.^[20] in Figs.7-10.

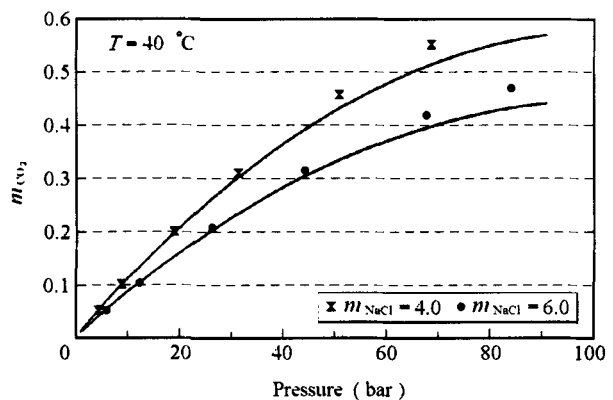


Fig.1 Solubility of carbon dioxide in aqueous solution of sodium chloride at $T = 40^\circ C$. Experimental results are from Nicolaisen^[2]

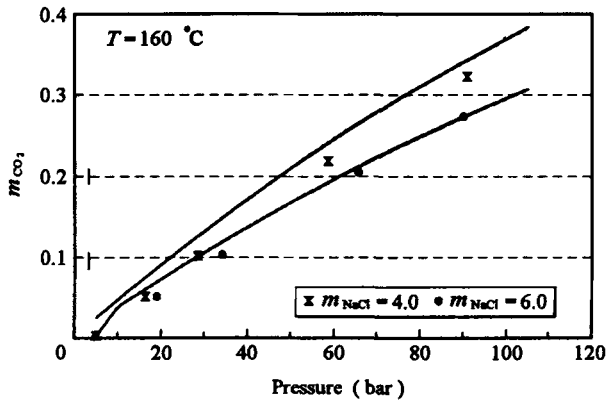


Fig.2 Solubility of carbon dioxide in aqueous solution of sodium chloride at $T = 160^\circ$. Experimental results are from Nicolaisen^[2]

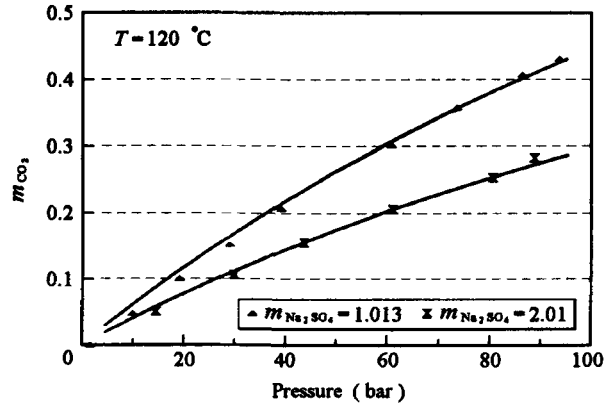


Fig.5 Solubility of carbon dioxide in aqueous solution of sodium sulfate at $T = 120^\circ\text{C}$. Experimental results are from Rumpf and Maurer^[19]

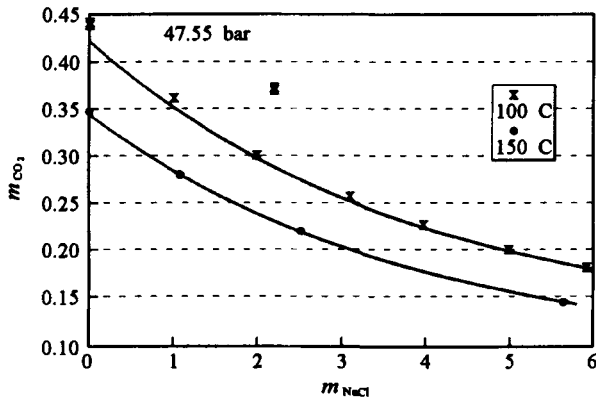


Fig.3 Solubility of carbon dioxide in aqueous solution of sodium chloride at $P = 47.55$ bar. Experimental results are from Malinin and Kurovskaya^[21]

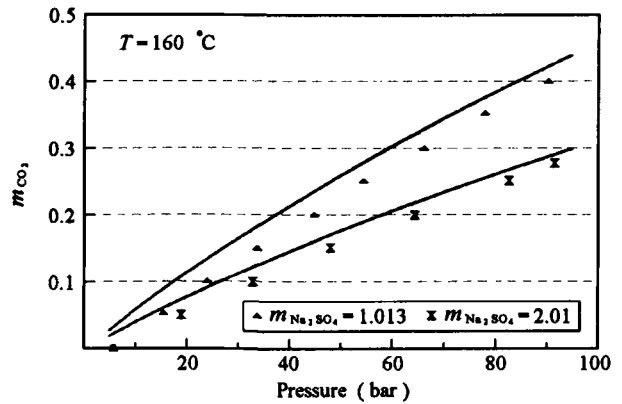


Fig.6 Solubility of carbon dioxide in aqueous solution of sodium sulfate at $T = 160^\circ\text{C}$. Experimental results are from Rumpf and Maurer^[19]

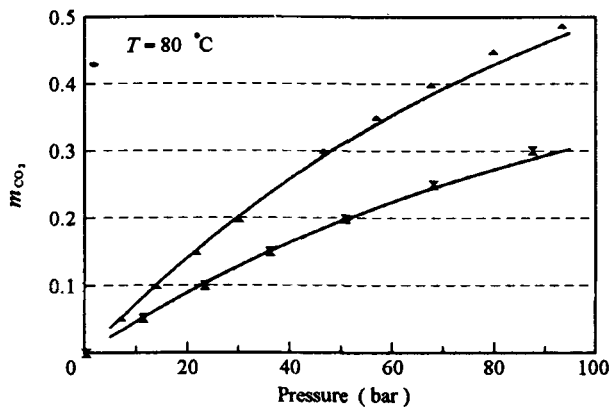


Fig.4 Solubility of carbon dioxide in aqueous solution of sodium chloride at $T = 80^\circ\text{C}$. Experimental results are from Rumpf and Maurer^[19]

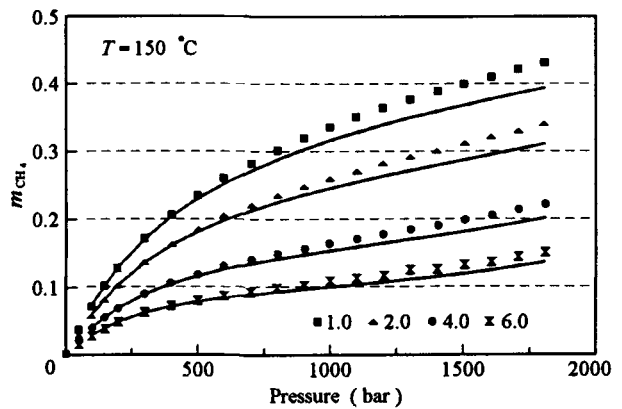


Fig.7 Solubility of methane in aqueous solution of sodium chloride at $T = 150^\circ\text{C}$ compared to data from Duan et al.^[20]

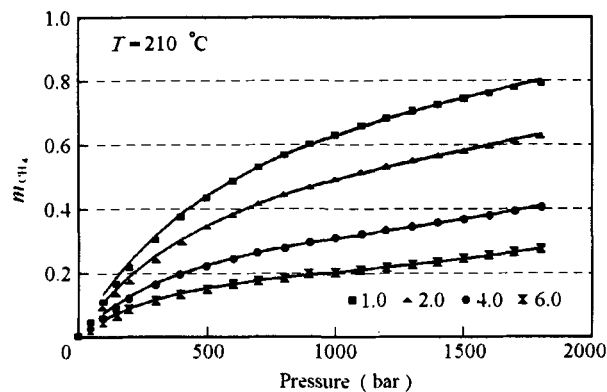


Fig.8 Solubility of methane in aqueous solution of sodium chloride at $T = 210^{\circ}\text{C}$ compared to data from Duan et al.^[20]

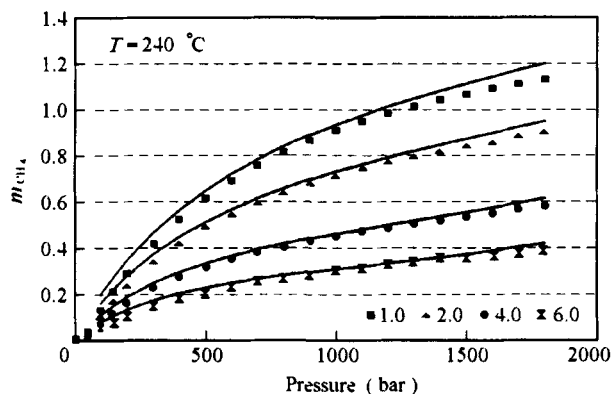


Fig.9 Solubility of methane in aqueous solution of sodium chloride at $T = 240^{\circ}\text{C}$ compared to data from Duan et al.^[20]

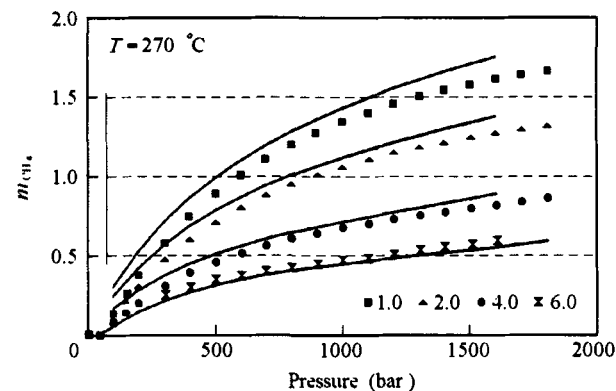


Fig.10 Solubility of methane in aqueous solution of sodium chloride at $T = 270^{\circ}\text{C}$ compared to data from Duan et al.^[20]

The «salting out» observed when sodium chloride or sodium sulfate is added to a mixture containing CO_2 or CH_4 is well predicted by the above procedure. The deviations observed are of the same order of

magnitude as the experimental ones (8%). The close agreement between our calculated gas solubilities and the experimental ones gives considerable support to the combination of modified HKF equations of state and Pitzer's ion interaction formalism.

CALCULATED H_2S SOLUBILITIES IN NaCl SOLUTION

Hydrogen sulphide is a frequent component of natural systems. As natural hydrothermal solutions usually contain appreciable concentrations of sodium chloride, accurate prediction of H_2S solubility in H_2O - NaCl is needed. Several experimental investigations on the above system have been carried out during the last decades^[1,22-25].

Barta and Bradley^[10] fitted the solubility data of Drummond^[1] to the semi-empirical interaction model of Pitzer. Their values were used by Barrett et al.^[24] to correlate their experimental data.

Barta and Bradley introduced in their expression molecule-molecule interaction parameters. Since in the two previous cases we neglected those contributions, according to Rumpf et al.^[11] and Duan et al.^[20] articles, in this work we propose new binary and ternary interaction parameters. Our values have been obtained by regression of Drummond data without any molecule-molecule contribution. This approximation seems to be reasonable as the molality of dissolved hydrogen sulphide remains small and leads to an expression involving 12 parameters instead of 15.

The following expressions are proposed for the binary, $\beta_{\text{H}_2\text{S},\text{Na}^+}^{(0)}$, and ternary, $\Gamma_{\text{H}_2\text{SNa}^+,\text{Cl}^-}$, interaction parameters:

$$\begin{aligned} \beta_{\text{H}_2\text{S},\text{Na}^+}^{(0)} &= 19.754092 - 0.20387763T \\ &+ 0.0008237638T^2 - 1.6230109 \times 10^{-6}T^3 \\ &+ 1.5594526 \times 10^{-9}T^4 - 5.8340662 \times 10^{-13}T^5 \\ \Gamma_{\text{H}_2\text{SNa}^+,\text{Cl}^-} &= -4.759142 + 0.049361213T \\ &- 0.00020040153T^2 + 3.9781484 \times 10^{-7}T^3 \\ &- 3.8618111 \times 10^{-10}T^4 + 1.4646191 \times 10^{-13}T^5 \end{aligned}$$

Vapor phase fugacity is calculated using the Peng-Robinson cubic equation of state as modified by Carroll et al.^[26], who introduced minor modifications to improve water-hydrogen sulphide vapor-liquid, liquid-liquid and liquid-liquid-vapor equilibrium prediction. This equation can only be used for temperatures between 42 and 240°C.

The following calculated curve illustrates our predicted solubilities. Experimental data are from Barrett et al.^[24].

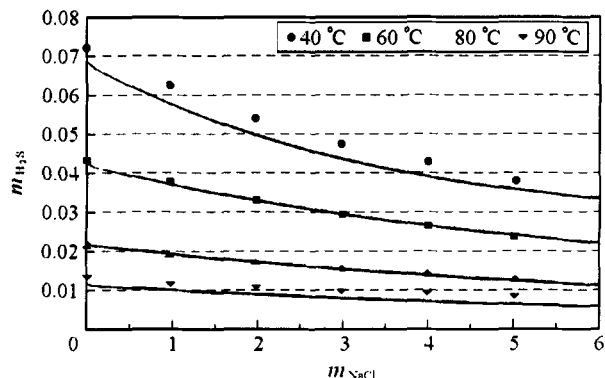


Fig.11 Influence of sodium chloride concentration on hydrogen sulphide solubility at $T = 40, 60, 80$ and 90°C . Experimental results are from Barrett et al.^[24]

Table 1 and 2 contains predicted H₂S solubility values and experimental data respectively from Drummond^[1] and Suleimenov and Krupp^[25], and the absolute relative deviation.

Table 1 Calculated and experimental H₂S solubility in NaCl solution. (Experimental data are from Suleimenov and Kupp^[25])

T (°C)	P (bar)	$Y_{\text{H}_2\text{S}}$	m_{NaCl}	$m_{\text{exp H}_2\text{S}}$	$m_{\text{calc. H}_2\text{S}}$	$A.R.D.$ %
155.30	11.96	0.5377	0.5014	0.152	0.147	3.04
155.20	12.14	0.5519	0.9175	0.147	0.142	3.73
155.30	12.37	0.5641	1.2665	0.145	0.139	4.56
155.40	12.65	0.5767	1.5652	0.144	0.138	4.50
155.40	12.92	0.5888	1.8138	0.145	0.138	4.84
155.40	13.12	0.5980	2.0320	0.148	0.137	7.45
155.30	13.42	0.6103	2.2240	0.150	0.138	7.77
155.30	13.71	0.6204	2.3911	0.154	0.140	9.04
155.20	14.05	0.6320	2.5400	0.158	0.143	9.60
216.50	27.60	0.2084	0.2353	0.132	0.136	2.92
216.50	27.58	0.2189	0.6336	0.127	0.131	3.26
216.40	27.46	0.2266	0.9638	0.127	0.126	0.74
216.30	27.43	0.2351	1.2445	0.127	0.123	2.60
216.30	27.48	0.2432	1.4858	0.128	0.122	4.17
216.40	27.56	0.2498	1.6932	0.130	0.121	6.96
216.30	27.70	0.2597	1.8787	0.131	0.122	6.92
216.30	27.87	0.2684	2.0434	0.133	0.123	7.94

total mean absolute relative deviation: 5.3%

where $A.R.D.$ is the absolute relative deviation, given by:

$$A.R.D. = |m_{\text{exp.}} - m_{\text{calc.}}| / m_{\text{exp}} \times 100$$

and the total mean absolute deviation

$$= \sum_{n=1}^N \left(\frac{|m_{n,\text{exp.}} - m_{n,\text{calc.}}|}{m_{n,\text{exp.}}} \times 100 \right)$$

Table 2 Calculated and experimental H₂S solubility in NaCl solution. (Experimental data are from Drummond^[1])

T (°C)	P (bar)	$Y_{\text{H}_2\text{S}}$	m_{NaCl}	$m_{\text{exp H}_2\text{S}}$	$m_{\text{calc. H}_2\text{S}}$	$A.R.D.$ %
41	8.965	0.991	1	0.497	0.505	1.63
48	9.411	0.988	1	0.484	0.473	2.18
51	9.796	0.987	1	0.478	0.470	1.76
56	10.201	0.984	1	0.469	0.453	3.31
61.10	10.515	0.981	1	0.461	0.431	6.51
71.10	11.518	0.972	1	0.444	0.414	6.85
81.10	12.480	0.960	1	0.427	0.395	7.51
91.20	13.513	0.946	1	0.412	0.379	8.10
101.20	14.486	0.959	1	0.388	0.376	3.04
111.30	15.651	0.926	1	0.382	0.363	5.10
136	18.892	0.839	1	0.378	0.341	9.85
161.50	23.481	0.739	1	0.368	0.341	7.24
176.60	27.240	0.675	1	0.366	0.352	3.88
191.70	31.514	0.606	1.01	0.372	0.362	2.74
201.70	35.100	0.562	1.01	0.373	0.374	0.38
216.80	41.158	0.495	1.01	0.382	0.392	2.68
226.90	45.990	0.453	1.01	0.389	0.407	4.58
231.90	48.543	0.432	1.01	0.395	0.413	4.53
237	51.167	0.410	1.01	0.404	0.418	3.54
242	54.196	0.391	1.02	0.408	0.428	4.92
41	6.969	0.954	2	0.340	0.344	1.10
46	7.314	0.954	2	0.333	0.335	0.74
51	7.658	0.954	2	0.327	0.322	1.65
56	7.993	0.954	2	0.321	0.319	0.78
76.10	9.786	0.950	2	0.295	0.290	1.63
86.20	10.404	0.955	2	0.280	0.277	1.02
106.20	12.136	0.956	2	0.274	0.254	7.25
139.40	15.934	0.956	2	0.267	0.230	13.99
171.60	21.881	0.954	2.01	0.263	0.230	12.64
196.70	28.617	0.949	2.01	0.262	0.241	8.08
226.90	40.611	0.910	2.02	0.278	0.265	4.70
277.30	74.537	0.928	2.06	0.304	0.322	5.89
41	8.894	0.941	4	0.361	0.341	5.48
54	10.140	0.940	4	0.339	0.328	3.19

<i>T</i> (°C)	<i>P</i> (bar)	<i>Y</i> H ₂ S	<i>m</i> NaCl	<i>m</i> _{exp} H ₂ S	<i>m</i> _{calc.} H ₂ S	<i>A.R.D.</i> %
56	10.474	0.940	4	0.331	0.330	0.30
76.10	12.480	0.941	4	0.306	0.302	1.41
84.60	13.311	0.941	4	0.299	0.288	3.55
86.20	13.513	0.941	4	0.296	0.287	3.05
96.20	14.557	0.942	4	0.290	0.273	6.03
118.30	17.039	0.944	4	0.283	0.245	13.59
151.50	22.063	0.944	4.01	0.263	0.228	13.33
181.60	28.678	0.942	4.01	0.264	0.234	11.53
201.70	34.888	0.940	4.02	0.264	0.244	7.58
226.90	45.170	0.935	4.03	0.270	0.270	0.12
237	50.123	0.933	4.03	0.276	0.278	0.65
242	53.527	0.931	4.03	0.279	0.291	4.30
41	8.550	0.991	6	0.294	0.280	4.86
46	8.965	0.989	6	0.288	0.272	5.41
51	9.451	0.986	6	0.281	0.267	5.09
57	10.069	0.983	6	0.271	0.260	3.95
61.10	10.485	0.980	6	0.265	0.255	3.61
66.10	10.971	0.976	6	0.259	0.249	3.92
71.40	11.376	0.972	6	0.256	0.248	3.20
76.10	11.862	0.966	6	0.251	0.234	6.71
86.20	13.240	0.945	6	0.242	0.225	6.93
94.20	13.929	0.935	6	0.237	0.215	9.46
101.20	15.327	0.937	6	0.211	0.219	3.71
111.30	15.823	0.936	6	0.213	0.201	5.51
136.40	18.609	0.867	6.01	0.215	0.183	14.88
166.50	24.059	0.765	6.01	0.206	0.179	12.97
186.70	28.749	0.687	6.02	0.206	0.183	11.02
201.70	33.439	0.628	6.02	0.202	0.192	4.92
216.80	38.889	0.566	6.03	0.204	0.203	0.49
221.90	40.966	0.545	6.03	0.205	0.207	1.12
226.90	43.093	0.524	6.03	0.207	0.211	2.03
231.90	45.372	0.503	6.04	0.209	0.215	2.97

total mean absolute relative deviation: 5.1%

Our solubility data compare closely with literature values over the range of investigation. Departure from experimental data can be compensated by regression of HKF equations of state parameters. This remains to be undertaken but seems to be necessary to improve the previous results in the range of temperature from 100 to 180°C.

CONCLUSION

Thermodynamic properties and phase behaviour of aqueous salt mixtures at high temperature and pres-

sure could be calculated using a combination of the HKF equations of state and the Pitzer model. In the present study, methane, carbon dioxide and hydrogen sulphide vapor-liquid equilibrium in electrolyte solutions at high pressure and high temperature were investigated. For the H₂S-H₂O-NaCl system, new Pitzer binary and ternary parameters are proposed. The good agreement between both mineral and gas solubilities calculated using the previous model confirm the accuracy of the above method. The proposed procedure, based on models which have theoretical justifications, could be used to calculate thermodynamic properties of systems formed with hydrocarbons, water and salts, including minor and trace elements. It is an approach suitable for simulating the behaviour of certain mixtures encountered in the petroleum industry. Moreover it presents the advantage of doing more than simply smoothing experimental data.

Acknowledgements

We would like to thank Dr.H.Zhou (Elf Aquitaine Production) for useful discussions on this work. We are also indebted to ELF AQUITAINE society for financial support.

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