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Thermodynamic model of aqueous CO₂–H₂O–NaCl solutions from -22 to $100 \,^\circ$ C and from 0.1 to $100 \,\text{MPa}$

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ABSTRACT

Experimental measurements of the solubility of CO₂ in aqueous NaCl solutions have been assembled from 21 literature studies and tested for consistency using analytical and thermodynamic criteria. Of the 508 data compiled, 170 data (33%) were discarded and 36 were reserved to test the high-pressure dependency of the model. Possible reasons for the observed discrepancies between datasets are discussed. The 302 measurements that satisfy the acceptance criteria have been used to fit Pitzer parameters. These have been incorporated into a semi-empirical, $\gamma - \phi$ type thermodynamic model that builds upon published equations of state for the unary and binary subsystems. The accepted experimental solubilities are reproduced by the model with a precision of better than 1.6% (one standard deviation) over the entire P-T-xrange considered. The new model provides a thermodynamically consistent description of numerous properties of the aqueous liquid in the ternary CO2-H2O-NaCl system, including: the activity coefficients, activities and partial molar volumes of CO_{2(aq)} and Na⁺Cl⁻(aq); the activity coefficient and osmotic coefficient of the solvent H₂O; the Setchenow coefficient; saturation indices of all four solid phases in the system (CO₂-clathrate-hydrate, ice, hydrohalite and halite); and the molar volume, excess molar volume and density of the bulk liquid. These properties can be calculated for any CO₂ concentration up to saturation, and for any NaCl concentration (whether stable or metastable). The model is available as a computer code at <www.geo.unibe.ch/diamond>.

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1. Introduction

Accurate knowledge of the thermodynamic properties of aqueous solutions containing CO_2 and NaCl has become essential to many branches of technology. Among these are industries dealing with the production of petroleum and gas, including enhanced oil recovery, desalination of seawater, supercritical fluid extraction and oxidation, fertilizers and treatment of waste water. In the geosciences the ternary CO_2-H_2O -NaCl system is recognized to be an important model of the chemically more complex fluids that are present in the subsurface of the earth. Geoscience fields that make use of such models include geothermal energy, permafrost, hydrothermal ore deposits, fluid inclusions in minerals, and geological sequestration of anthropogenic emissions of CO_2 .

Several models of the $CO_2-H_2O-NaCl$ system at moderately elevated *T*–*P* conditions have been published. For example, the group of equations of state (EoS) by Duan et al. [1–4] are semiempirical descriptions of CO_2 solubility and of solution density up to halite saturation at temperatures (*T*) of $0-260 \,^{\circ}C$ and pressures (*P*) of 0–200 MPa. Spycher et al. [5,6] present a solubility model for aqueous solutions with up to 6 molal NaCl and 4 molal CaCl₂ at conditions of 12–100 °C and 1–60 MPa. Other models are by Kiepe et al. [7], Papaiconomou et al. [8], Dubessy et al. [9] and Ji et al. [10]. All of these have their strengths and weaknesses. The less empirical models offer more versatility and reliability in extrapolation, but usually at the expense of accuracy.

In the present study we evaluate experimental studies in the literature and develop a semi-empirical model with the emphasis on accuracy. We extend our previous study [11], which evaluated the published experimental data on the solubility of CO₂ in pure liquid water at temperatures between -1.5 and $100 \,^{\circ}$ C and at pressures between 0.1 and 100 MPa. The resulting semi-empirical, $\gamma - \phi$ type of model serves to describe the CO₂-H₂O subsystem in the new ternary model. The EoS of Pitzer et al. [12] is incorporated in the new model for the binary H₂O–NaCl subsystem.

In the following we first outline the pertinent phase relations in the $CO_2-H_2O-NaCl$ system up to 100 °C and 100 MPa. Experimental data on CO_2 solubility are then collated from the literature and criteria are established to discriminate reliable from unreliable values. All the data are then filtered with respect to these criteria by means of the Setchenow equation. The retained data are next used to fit parameters for Pitzer's formalism of the solutes. This yields an accurate thermodynamic description of the ternary aqueous solu-

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0 1 MPa isoba

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20

30

Fig. 1. *T*–*P* projection of stable phase relations in the CO₂–H₂O–NaCl system within the low-*T*, low-*P* region of this study. Phase boundaries are valid for saturation with respect to a carbonic fluid (vapour, liquid or supercritical). Aqueous liquid is stable only in the unshaded area of the diagram. Quintuple point 1 (system eutectic) marks the lowest temperature at which aqueous liquid is stable. Dot-dashed curves show boundaries of ice and clathrate in the binary CO₂–H₂O subsystem. Blue continuous curves pertain to bulk compositions with NaCl concentrations between 0 and 5 molal (symbol b_{NaCl} in legend); peritectic curve (red) pertains to compositions above 5 molal. CEP is a critical end-point of the system. All the curves (except that at *T* below point 1) are calculated from the model in this study. Dashed lines locate three of the isobaric sections plotted in Fig. 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

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0

tion including its various phase boundaries. Finally, we present a selection of calculations that illustrate the predictive capacity of the new model.

10

8

7

6

5

4

3

2

1

0

+ V

Ice + HH -20

Ice + L_{aq} + V

.....

-10

Pressure / MPa

2. Phase relations

This study focuses on the properties of aqueous solutions in equilibrium with a free CO₂-rich (carbonic) phase, whether in the vapour, liquid or supercritical state. Such a two-phase equilibrium is not stable over the entire compositional range of the CO₂-H₂O-NaCl system in the *T*-*P* region of interest. The compositional space occupied by the aqueous solution is severely restricted at low temperatures and at high NaCl contents by the saturation surfaces (liquidi) of four solid phases: ice (H₂O), hydrohalite (NaCl·2H₂O), halite (NaCl) and CO₂-clathrate-hydrate (approximated by the formula CO₂·*n*H₂O, where *n* = 5.67-7.67). One of the tasks of this study is to map out the stability boundaries of the aqueous liquid.

Among all the mentioned phases in the $CO_2-H_2O-NaCl$ system, aqueous liquid is the only true ternary phase, in that it may dissolve sufficient CO_2 and NaCl to fundamentally alter its thermodynamic properties and its phase relations. In contrast, carbonic fluid² in equilibrium with aqueous liquid is a degenerate binary phase. Over the *T*–*P* range of interest the solubility of NaCl in the carbonic fluid is essentially nil. The presence of NaCl in the aqueous liquid has no measurable effect on the *T*–*P* locus of the three-phase equilibrium between aqueous liquid, carbonic liquid and carbonic vapour [13]. However, the carbonic phases dissolve small amounts of H₂O; the solubility increases with *T* and *P* to reach a maximum of 2 mol% at 100 °C and 100 MPa [11]. At *T*–*P* conditions along the three-phase curve the H₂O content of the carbonic phase is less than 0.4 mol%. This shifts the *T*–*P* locus of the curve by only a tiny amount compared to the liquid–vapour curve of pure CO_2 . The isothermal pressure shift is at most 0.045 MPa, or 0.6% at 7.3 MPa, and the *T–P* values of the critical point increase by approximately 0.4 °C and 0.033 MPa [14]. Nevertheless, the H₂O content of the carbonic fluid has an appreciable affect on the fugacity of CO_2 and so it must be incorporated in any thermodynamic model. None of the four solid phases exhibits multicomponent solid-solution behaviour within the ternary system, and clathrate is the only non-stoichiometric solid among them.

 $0 < b_{\text{NaCl}} < 5$ $b_{\text{NaCl}} > 5$

.....

50

40

Fig. 1 shows projected phase boundaries in the low-*T*, low-*P* portion of the region covered by the present work. Concentrations of NaCl are indicated in the legend with the symbol b_{NaCl} , which denotes the molality of the undissociated salt. The fields between phase boundaries are labelled with the stable phase assemblages. Aqueous liquid (L_{aq}) is stable only in the unshaded region of the diagram. The lowest temperature at which aqueous liquid is stable is at quintuple point 1, the system eutectic, where the solution is in equilibrium with hydrohalite (HH), clathrate (Cla), ice and carbonic vapour (V). Two of the quadruple curves that emanate from this point are part of the system solidus, which delineates the stability field of aqueous liquid.

The three-phase curve involving aqueous liquid, carbonic liquid (L_{car}) and carbonic vapour runs diagonally through the centre of Fig. 1, from the critical end-point (CEP) at 31.5 °C and 7.41 MPa [14], down to -25 °C and 1.68 MPa [15]. Above this curve, carbonic liquid is the phase that saturates the aqueous liquid, whereas below it, vapour is the saturating phase. At *T*–*P* conditions above the CEP, aqueous liquid is in equilibrium with supercritical carbonic fluid (SCF_{car}).

All the phase boundaries drawn in Fig. 1 are projections from the CO_2-H_2O -NaCl compositional axes. Thus, the stability of clathrate in equilibrium with aqueous liquid+carbonic fluid extends from its locus in the CO_2-H_2O subsystem (dot-dash curves emanating from binary Q_2) down to the solidus, where the aqueous liquid contains about 5 molal NaCl. The CO_2 -saturated liquidus of ice similarly stretches from the dot-dashed curve at pressures below

² Throughout the text, chemical formulae are used only to denote thermodynamic components (e.g. CO_2 , H_2O and NaCl). To avoid confusion, all phases are referred to by their proper names. Thus, CO_2 -liquid is termed "carbonic liquid" and so on.

Table 1 Studies of CO $_2$ solubility in aqueous NaCl solutions from 0 to 100 $^\circ C$ and from 0.1 to 100 MPa.

Reference	P(MPa)	T (°C)	$b_{\rm NaCl} ({\rm mol/kg_{H_2O}})$	Data	P-T-x accuracy	Dev. (%) ^a	At <i>T</i> (°C)	w ^b	Criteria for weight
Setchénow [16]	0.101	18.2	0.2-6.1	9	$x_{CO2(aq)} \pm 1\%$	9.1	18.2	0.25	Non-reversed experiments
Markham and Kobe [17]	0.1	0.2-40	0.1-4.0	15	$P\pm0.04\%$	-0.6	0.2	1.0	Reversed experiments
					$T \pm 0.1 ^{\circ}C$ $x_{CO2(aq)} \pm 0.06\%$	-1.8 -5.0	25 40	1.0 0.75	
Harned and Davis [18]	0.101	0.1–50	0.2–3	92	$x_{\rm CO2(aq)} \pm 1\%$	-0.7 -0.4	0 5 10	0.75 0.75 0.75	Non-reversed experiments
						-1.2 -1.3	15 20	0.75 0.75 0.75	
						-0.7 -1.2	25 30	0.75 0.75	
						-1.7 -1.6 -1.0	35 40 45	0.75 0.75 0.75	
						-2.2	50	0.75	
Rosenthal [19]	0.101	20	1.6-5.7	3	$T \pm 0.2 \degree C$ $x_{CO2(aq)} \pm 0.9\%$	-5.3	20	0.75	Reversed experiments
Yeh and Peterson [20]	0.101	25–45	0.155	4	<i>P</i> ±0.03%	-0.4	25	0.5	Non-reversed; Short equilibra-tion time
					$T \pm 0.5 ^{\circ}\mathrm{C}$ $x_{\mathrm{CO2(aq)}} \pm 0.2\%$	0.5 2.0 5.6	30 37 45	0.5 0.5 0.25	
Gerecke [22]	0.101	15–60	0.5-4.8	38		-1.8	15	0.5	Non-reversed; Short equilibration time; for data ≥40°C, ln(b°/b) does not tend to zero
						-4.0	20	0.5	10 2010
						-3.0	25	0.5	
						-2.4	30	0.5	
						-0.3	40	0.5	
						-2.8	45	0.25	
						-3.6	50	0.25	
						-5.0	55	0	
						-2.3	60	0.25	
Onda et al. [23]	0.1	25	0.5–3.2	8	$T \pm 0.01 ^{\circ}\text{C}$ $x_{\text{CO2(aq)}} \pm 0.17\%$	-2.1	25	0.75	Non-reversed experiments
Malinin and Savelyeva	4.9	25–75	0.4-4.5	13	$P \pm 1\%$	-2.4	25	1.0	Reversed experiments
[27]					$T \pm 0.1 ^{\circ}\text{C}$ $x_{\text{CO2(aq)}} \pm 0.5\%$	-4.1 -5.0	50 75	1.0 0.75	
Malinin and Kurovskava [25]	4.9	25, 100	1–5.9	22	$P\pm1\%$	-3.2	25	1.0	Reversed experiments
					$T \pm 0.1 ^{\circ}\text{C}$ $x_{\text{CO2(aq)}} \pm 0.5\%$	-6.3	100	0.75	

Yasunishi and Yoshida	0.101	15-35	0.5–5.5	27	<i>T</i> ±0.05 °C	0.1	15	0.75	Non-reversed experiments
[20]						2.4 3.7	25 35	0.75 0.75	
Drummond [28]	3.5-6.9	20-100	1-6	92	<i>P</i> ±0.03 MPa	-10.9	30.7	0	Partly reversed experiments; short equilibration time; low precision
					<i>T</i> ±0.25 °C	-10.6 0.5 -4.2 9.6 11.1	36.3 37.6 45 48 58.9	0 0 0 0	
						-9.6 -9.1 -9.0 -5.9	69.7 79.2 83.2 90	0 0 0 0	
						$-10.0 \\ -5.4$	97.4 100	0 0	
Cramer [29]	0.8–1.9	0-100	0.5-4.9	18	$P\pm0.07\mathrm{MPa}$	-0.9	0	0.5	Non-reversed; low stated precision.
					$T \pm 0.2 ^{\circ}\text{C}$	-3.1	20	0.5	Author's smoothed data used for <i>k</i> _H only
					$x_{CO2(aq)} \pm 3-8\%$	-4.9 -6.4 -7.2 -7.4	40 60 80 100	0.25 0.25 0.25 0.25	
Nighswander et al. [30]	4–10	80	0.17	8	P±0.035 MPa T+0.4°C	2.6	80	0	Non-reversed; low precision; <i>P</i> -trend contradicts [31,32]
					$x_{CO2(aq)} \pm 7\%$				
He and Morse [33]	0.004-0.1	0–90	0.1-6.1	31	$T \pm 0.1 ^{\circ}\mathrm{C}$ $x_{\mathrm{CO2(aq)}} \pm 1\%$	No data		0	No binary CO ₂ –H ₂ O data measured; Irregular trends in data (e.g.
									45–50 °C)
Rumpf et al. [34] and Nicolaisen [31]	0.5–9.6	40-80	4–6	38	<i>P</i> ± 3% at <i>P</i> < 6 MPa and ±5% at <i>P</i> > 6 MPa <i>T</i> ±0.1 °C	2.0	50	1	Experiments made with close approximation to reversal
Vasquez et al. [36]	0.101	20-35	0.7–2.9	16	$P \pm 0.2\%$ $T \pm 0.05 ^{\circ}\text{C}$ $x_{\text{CO2(aq)}} \pm 0.7\%$	-3.1 -0.6 1.5 3.4	20 25 30 35	0.75 0.75 0.75 0.75	Non-reversed
Zheng et al. [38]	0.05-0.09	5–65	0.7–3.3	18	P±0.3% T±0.1°C	-0.5 -0.3 -0.5 -0.5 -1.3	5 30 35 60 65	0.75 0.75 0.75 0.75 0.75	Non-reversed

Reference	P (MPa)	$T(^{\circ}C)$	$b_{\rm NaCl} ({ m mol/kg}_{ m H_20})$	Data	P-T-x accuracy	Dev. (%) ^a	At T (°C)	qM	Criteria for weight
Kiepe et al. [7]	0.007-	10 40, 80	0.5-4.3	64	$P\pm 1.5{-}0.2\%$	6.0 ^c	40	0	Non-reversed;
					$T\pm 0.01$ °C	-7.1 ^c	80	0	Short equilibration time; For
									80 °C data, $\ln(b^\circ/b)$ does not
									tend to zero. For 40°C data,
									P-trend contradicts [31,32]
						-6.2 ^c	100	0	
Bando et al. [41]	10-20	30-60	0.18-0.56	36	$x_{CO2(aq)} \pm 0.4-3.1\%$	-2.5	30	Data not used to fit model	Non-reversed
						-6.1	40		
						-3.8	50		
						-0.9	60		
Koschel et al. [42]	5-20	50, 100	1,3	14	$P\pm0.3-0.4\%$	2.7	50	0.5	Non-reversed;
					$T \pm 0.01 ^{\circ}\text{C} x_{\text{CO2(aq)}} \pm 7\%$	3.7	100	0.5	Low precision
^a Relative deviation (%) of	the experiment	tal CO ₂ solubil.	ity (x_{exp}) in the binary CO)2-H2O syste	$\frac{1}{2}$ m from the model solubility (x	v _{mod}) according	to [11]. Calculat	ed as dev. = $(x_{exp} - x_{mod})/x_{mod} \times 10^{-10}$	00 for data measured at T indicated in

Deviation based on comparison of Henry's constants in Ref. [7] compared to model values in Ref. [11].

Relative weight used in model fitting, from Table

20 CO₂-saturated aqueous liquid 10 Femperature / °C -10 Saturated in carbonic liquid -20 Saturated in carbonic vapour 2 0 3 4 5 6 Aqueous salinity (b_{NaCl}) / molkg H₂O⁻¹

Fig. 2. Stability limits of CO₂-saturated aqueous liquid in the low temperature portion of the CO₂-H₂O-NaCl system. Curves are isobaric liquidi (saturation boundaries) of the 4 solids in the system. Dots are quadruple points: Q_1 , Q_2 , isobaric eutectics (E) and peritectics (P). The isobars illustrate the range in phase relations that occur within the system up to 100 MPa. Three of the isobars are marked in Fig. 1 to aid understanding. Colours of quadruple points correspond to colours of curves in Fig. 1. It can be seen that increasing the CO₂ pressure expands the thermal stability of clathrate, hydrohalite and halite, thereby reducing the stability field of aqueous liquid. All features are calculated from the model in this study.

 Q_1 , down to the solidus. At NaCl concentrations above about 5 molal, hydrohalite is stable in equilibrium with CO₂-saturated L_{aq} throughout the *T*–*P* interval between the solidus and the vertical peritectic curve (red). On this curve hydrohalite reacts to halite upon heating. Depending on the aqueous salinity, the upper temperature limit of the CO₂-saturated halite liquidus may lie below 100 °C (an example is given for 6 molal NaCl in Section 5.1 below) or at much higher temperatures.

The compositional variations projected into the T-P plane in Fig. 1 are difficult to visualize. To aid understanding, Fig. 2 shows four isobaric sections which illustrate the variety of phase relations encountered as a function of aqueous NaCl concentration. The three isobars at 0.1, 0.9 and 4 MPa fall within the pressure range of Fig. 1 (indicated by horizontal dashed lines in Fig. 1); the 100 MPa isobar displays the relationships at the maximum pressure of this study. All the curves in Fig. 2 are liquidi that involve three phases: a solid plus aqueous liquid and the omnipresent, saturating carbonic fluid. Along each isobar, aqueous liquid is stable at temperatures above the liquidus curves. Thus, the liquidi constrain the stability of aqueous liquid, the lowest temperature on each isobar being a quadruple eutectic point (E in Fig. 2). Other quadruple points that develop at the junction of the liquidi include isobaric peritectics (P in Fig. 2) and the cotectics involving clathrate, which are commonly referred to as Q_1 and Q_2 .

Under conditions of CO_2 -saturation, the phase relations of the aqueous liquid above 50 °C and above 10 MPa (i.e. outside Fig. 1) are simple. The halite liquidi at elevated NaCl molalities, as visible in Fig. 2, continue through to 100 °C and further. The solidus and peritectic curves rise steeply with slightly positive *P*/*T* slopes to 100 MPa.

The thermodynamic model that is developed in this study incorporates all the liquidi illustrated in Figs. 1 and 2. Indeed,

Table 2

Experimental methods of studies of CO₂ solubility in aqueous NaCl solutions from 0 to 100 °C and from 0.1 to 100 MPa.

Reference	Method	Approach to equilibrium	Equilibration time
Setchénow [16] Markham and Kobe [17]	Ostwald; agitation by shaking Ostwald; known volume of CO_2 gas set in contact with known mass of aq. solution at fixed <i>P</i> and <i>T</i> ; reduction of $V(CO_2)$ measured upon equilibration; agitation by shaking	CO ₂ dissolution into undersat. aq. solution Reversed from high and low <i>P</i> _{CO2}	Not stated 20 min
Harned and Davis [18]	CO_2 gas brought near to saturation with H_2O vapour prior to solubility experiment; CO_2-H_2O gas mixture dissolved into known mass of liquid solution; agitation by bubbling and rocking; dissolved CO_2 determined by titration	CO ₂ -H ₂ O gas mixture dissolved into undersat. aq. solution	Approx. 12 h
Rosenthal [19] Yeh and Peterson [20]	Ostwald; agitation by shaking Ostwald; agitation by stirring. Details in Ref. [21]	Reversed from high and low P_{CO_2} CO ₂ dissolution into undersat. aq. solution	Not stated Approx. 30 min
Gerecke [22]	Ostwald; agitation by stirring	Lowest <i>T</i> equilibration by CO ₂ dissolution into undersat. aq. solution; all other runs via CO ₂ exsolution from oversat. aq. solution	30 min
Onda et al. [23] Malinin and Savelyeva [24]	Ostwald; agitation by stirring Open-system cell at fixed <i>P</i> and <i>T</i> ; CO ₂ gas bubbled through aq. solution; solution sampled and degassed; CO ₂ absorbed by KOH and determined gravimetrically	CO ₂ dissolution into undersat. aq. solution Partly reversed; partly via CO ₂ dissolution into undersat. water, partly via CO ₂ exsolution from oversat. water	Not stated 48 h at 25–50 °C; 24 h at 75 °C
Malinin and Kurovskaya [25]	See [24]	Mostly via CO ₂ dissolution into undersat. aq. solution; partly via CO ₂ exsolution from oversat. aq. solution; partly reversed	48 h at 25–50 °C; 24 h at 75 °C
Yasunishi and Yoshida [26]	Ostwald; agitation by stirring. Details in Ref. [27]	CO2 dissolution into undersat. aq. solution	Not stated
Drummond [28]	Known masses of CO ₂ and aq. solution enclosed in rocking autoclave of known <i>V</i> . Pressure of CO ₂ vapour above solution was measured as a function of <i>T</i> upon progressive heating or cooling. $x_{CO2(aq)}$ calculated from P_{CO2}	CO ₂ exsolution from oversat. aq. solution upon heating; CO ₂ dissolution into undersat. aq. solution upon cooling	Approx. 8 min per datum
Cramer [29]	CO_2 gas introduced into stirred aq. solution at <i>P</i> , <i>T</i> ; solution sampled at constant <i>P</i> , <i>T</i> ; solution decassed and CO_2 measured volumetrically	CO ₂ dissolution into undersat. aq. solution	24 h
Nighswander et al. [30]	CO ₂ gas in adjustable-volume cell equilibrated with stirred aq. solution; solution sampled then degassed and CO ₂ analysed volumetrically	Highest-P equilibration by CO ₂ dissolution into undersat. aq. solution; all other runs via CO ₂ exsolution from oversat. solution	12 h upon attainment of const. <i>P</i>
He and Morse [33]	Equilibration of CO_2 with stirred aq. solution followed by gas chromatographic analysis of $\frac{V}{V}(2\pi)$	CO ₂ dissolution into undersat. aq. solution	Not stated
Rumpf et al. [34] and Nicolaisen [31]	Optical cell of known V and T filled with CO ₂ gas; P measured; aq. solution added via calibrated high-P displacer until all CO ₂ dissolved; solution removed stepwise to reduce P until bubble-pt. encountered; $P_{\text{bubble-pt.}}$ measured; agitation by stirring. Details in Ref. [35]	<i>Initially</i> CO ₂ dissolution into undersat. aq. NaCl solution until all CO ₂ dissolved, <i>then P</i> reduction until bubble-point reached; i.e. exsolution from oversat. aq. solution	Not stated
Vasquez et al. [36]	Ostwald; agitation by stirring. Details in Vasquez [37]	CO2 dissolution into undersat. aq. solution	3-4 h
Zheng et al. [38] Kiepe et al. [7]	Ostwald; agitation by stirring Static cell: <i>P</i> measured at fixed bulk composition and <i>T</i> ; solubility calculated from liquid density measured by vibrating tube densimeter; agitation by stirring Details in Refs. [20:40]	CO_2 dissolution into undersat. aq. solution CO_2 dissolution into undersat. aq. solution	Not stated 30–45 min
Bando et al. [41]	Open-system cell of CO ₂ at fixed <i>T</i> ; aq. solution pumped stepwise into stirred CO ₂ until exp. <i>P</i> attained; equilibrated aq. solution extracted to sampling chamber, degassed and cooled to 0°C; $x_{CO2(aq)}$ calculated from measured <i>P</i> , <i>V</i> and mass of sampling chamber, using salting-out parameter for 0°C	CO2 dissolution into undersat. aq. solution	Several cycles each of 3 h
Koschel et al. [42]	CO_2 solubility deduced from limit of enthalpy of mixing ($\Delta_{mix}H_m$) as a function of $x_{CO2(aq)}$	CO ₂ and aq. solution simultaneously injected into a mixing cell within a calorimeter at fixed <i>P</i> , <i>T</i>	Not stated

the final model was used to calculate all the plotted curves representing equilibrium with aqueous liquid.

3. Published experimental data

For the T-P region of interest, 21 published studies were found. They report a total of 566 experimental measurements of the solubility of CO₂ in aqueous solutions of various salinities up to 6 molal NaCl. Table 1 lists the details in chronological order of publication. The studies span the period 1892–2006 and they encompass 13 different experimental methods, the most common being the Ostwald method (Table 2).

Fig. 3a and b displays the distribution of the available data in *T*–*P* and *T*– b_{NaCl} projections. Fig. 3c shows the data in a three-dimensional *T*–P– b_{NaCl} perspective. The phase boundaries of clathrate and ice in the binary CO₂–H₂O system are shown for reference (cf. Fig. 1). In all three diagrams, dots denote data used to constrain the parameters of the final thermodynamic model,



Fig. 3. $T-P-b_{NaC1}$ distribution of 386 experimental data on aqueous CO₂ solubility at P < 10 MPa considered in this study. Circles: 296 accepted data used to fit the final model (6 additional data at P > 10 MPa are not shown). Crosses: 78 discarded data (the remaining 92 discarded data from Ref. [28] are excluded for clarity). (a) T-NaCl molality projection. Continuous curve: ternary halite liquidus at 100 MPa. Dashed curve: ternary halite liquidus at 0.1 MPa. (b) T-P projection. Continuous curve: ternary $L_{aq} + L_{car} + V$ equilibrium. Dot-dashed curves: phase boundaries of ice and clathrate in the binary CO₂-H₂O subsystem (cf. Fig. 1).

and crosses denote data that were discarded at various stages of the evaluation and fitting procedure, as described below. Only the T–P–x region up to 10 MPa is well covered by the data, and even here the coverage at low temperature and high salinity is sparse. At higher pressure few measurements are available (30 data), the highest pressures reaching only 20 MPa.

3.1. Treatment of raw data

Some of the literature studies document all their replicate experimental measurements, whereas others list only averaged values for each set of intensive parameters (P, T, b_{NaCI}). Inasmuch as each replicate is a valid independent measurement we included them all in our data processing, making no distinction versus studies that report only averaged data. This choice carries a certain disadvantage. As the fit parameters for our thermodynamic model are ultimately obtained by a least-squares regression, the results are biased by the studies that contain the largest number of data (e.g. replicates), all other things being equal (e.g. T–P–x coverage, quality of data).

All the raw experimental data were recast into the molal scale. The CO₂ solubilities reported in the literature in terms of Ostwald, Bunsen and Kuenen coefficients were all recast into molalities using the reported raw data, rather than using the coefficients themselves. This was necessary because the authors' definitions often differ from those given in the IUPAC Solubility Data Series [43]. For example, the Ostwald coefficient is defined in Ref. [43] as the volume of saturating gas absorbed by a volume of pure solvent at *T* and *P*_{total} of the measurement. In the literature studies the data are often reduced to $T = 0 \circ C$, sometimes volumes of solution are used, sometimes partial pressure of CO₂ is used, and so on. The recalculation procedure for Ostwald coefficients is explained in Appendix A.

The present study follows the traditional approach of quantifying the salting-out of CO₂ by NaCl as a *relative* effect, i.e. by comparison with CO₂ solubility in the binary CO₂–H₂O system $(b^{\circ}_{CO_2})$. Thus, for the literature studies in which binary CO₂–H₂O data have been measured, we have used the *relative* $b^{\circ}_{CO_2}/b_{CO_2}$ values for the subsequent analysis. Fig. 4 shows all the collated experimental data in terms of ln $(b^{\circ}_{CO_2}/b_{CO_2})$, plotted as a function of NaCl molality and of temperature.

In line with this approach, Setchenow coefficients (k_{Sbb}) were calculated as follows:

$$k_{Sbb} \equiv \frac{1}{b_2} \ln \frac{b_1^0}{b_1}.$$
 (1)

Here, and henceforth in this study, subscript 1 denotes CO₂ and subscript 2 denotes NaCl. Thus, b_2 is the molality of NaCl in the solution; b_1^0 is the solubility of CO₂ (in mol/kg_{H₂O}) in the binary H₂O-CO₂ system and b_1 is the solubility of CO₂ (in mol/kg_{H₂O}) in the ternary CO₂-H₂O-NaCl system.

3.2. Discrimination of published experimental studies according to quality

Retrospective evaluation of the accuracy of solubility data is extremely difficult, as most of the reviewed experimental studies are ostensibly perfect; by virtue of the peer-review system they fulfil all the normal criteria of detailed description of methods, tests of reproducibility and checks of accuracy against existing literature. Nevertheless, the obvious disagreements between the datasets demonstrate that at least some of the studies are in error. As the disagreements are too large to permit meaningful averaging of the results, a judgement of data quality is an unavoidable step towards developing an accurate thermodynamic model.

For the present study a set of objective criteria has been established to discriminate the quality of the experimental data. These criteria are summarized in the column headings in Table 3 and described in the following. For each criterion a subjective (linear) scheme of relative weights has been adopted, such that the constraints on the subsequent fitting of the thermodynamic model reflect our assessment of data quality. Rather than applying the weighting scheme to each published dataset as a whole, the data



Fig. 4. Comparison of 446 experimental data on CO₂ solubility considered in this study. The ordinate shows the ratio of CO₂ solubility in the binary CO₂-H₂O system $(b_{CO_2}^{\circ} \text{ in mol/kg}_{H_2O})$ to that in the ternary system $(b_{CO_2}^{\circ} \text{ in mol/kg}_{H_2O})$, expressed as the natural logarithm. The values are plotted as a function of NaCl molality (b_{NaCl}) and temperature. Sixty-two data from Ref. [28] are omitted owing to lack of $b^{\circ}_{\rm CO_2}$ values. Curves: model predictions (this study) for the mean temperature of each T-range shown.

were divided into temperature intervals and each interval was then individually evaluated and weighted. The resulting weights are shown in Table 1 in the second column from the right. The rightmost column in Table 1 summarizes the specific justification for the weighting of each literature study.

Table 3

The primary criterion in Table 3 is based on the principle that any experimental study that yields accurate CO₂ solubilities in the ternary CO₂-H₂O-NaCl system should also yield accurate solubilities in the binary CO₂-H₂O system. All but one of the literature sources provide control measurements on the binary system, and so we have compared these measurements to the values given by the CO₂-H₂O model of Diamond and Akinfiev [11]. This model is actually founded in part on two of the studies considered in the present evaluation, namely Malinin and Savelyeva [24] and Malinin and Kurovskava [25]. The Diamond-Akinfiev model [11] reproduces a weighted subset of published binary experimental data with a standard deviation of 2%. Accordingly, in the present evaluation we place highest confidence in studies with binary data that deviate by less than 4% (i.e. 2 standard deviations) from the Diamond-Akinfiev model [11]. Data with higher deviations are assigned lower confidence levels. Thus, 5 classes of data quality have been distinguished with this criterion, as indicated in column 1 of Table 3. All the remaining discriminants of quality are applied to these classes.

The one study without any data on the CO₂-H₂O binary, that by He and Morse [33], was not considered further owing to the lack of this objective indicator of accuracy. Rather than measuring their own binary data, He and Morse adopted the indirect $k_{\rm H}$ values in Ref. [44]. Moreover, the reported ternary data display irregular trends as a function of NaCl concentration at $T > 45 \degree$ C, and the absolute values of the CO₂ solubilities are systematically lower than those of the other accepted studies (Fig. 4). Consequently, there appears to be no justification for using these data to constrain our model. The reason for the discrepancies in the results is unknown, but we note that He and Morse [33] were the only workers to measure CO₂ concentration by gas chromatography.

The second criterion in Table 3 reflects the way in which equilibrium was achieved in the ternary solubility experiments. The sluggish kinetics of equilibration between carbonic fluid and aqueous solutions at low temperatures is well known (e.g. [24]) and all the reviewed experimental studies duly reported that the reactants were thoroughly agitated prior to determining the solubility of CO_2 . However, only a subset of the studies demonstrated reversibility of the solubility values by changing the direction from which equilibrium was attained. Such reversals entail first measuring the apparent solubility upon progressive dissolution of CO₂ into an undersaturated solution. Then this value is checked against the apparent solubility observed under the same *P*–*T* conditions upon progressive exsolution of CO₂ from an oversaturated solution. The studies by Markham and Kobe [17], Rosenthal [19], Malinin and Savelyeva [24], Malinin and Kurovskaya [25], and Drummond [28] were carried out in this robust way, and the studies by Rumpf et al. [34] and Nicolaisen [31] were conducted in a manner closely approximating strict reversal. In the absence of other recognized problems, all these studies were assigned higher confidence, as indicated in column 2 of Table 3. The remainder of the studies were conducted

Relative weighting sch	eme for experimental data.				
Deviation from binary CO ₂ -H ₂ O model of [11] (%)	Weighting factors (applied in Table 1, column 9)				
	Reversed experiments	Non-reversed experiments with long or unstated equilibration times	Non-reversed with short equilibration times: [20], high-b _{NaCl} data of [22]; or low precision [28,29,42]	$ln(b^{\circ}/b)$ values for $b_{NaCI} \le 1$ do not tend to zero; [22] at $T \ge 40 \circ C$ [7] at $80 \circ C$	Partial molar volume of CO _{2(aq)} depends on pressure [7,30]
0-4	1	0.75	0.5	0.25	0
4.1-8	0.75	0.5	0.25	0	0
8.1-12	0.5	0.25	0	0	0
12.1-16	0.25	0	0	0	0
> 16	0	0	0	0	0
No data [33]	0	0	0	0	0

Table 4	
Equations used to test $P-T-b$ dependencies of Setchenow coefficien	its.

Fitting equati	on	Coefficients	Coefficients						
		<i>a</i> ₁	<i>a</i> ₂	<i>a</i> ₃	<i>a</i> ₄	<i>a</i> ₅	$\sigma_{abs(ksbb)}$		
First round of	fitting								
(4-1)	$a_1 + a_2 \frac{10^3}{T} + a_3 b_2$	0.051123	0.057184	-0.011934			0.016202		
(4-2)	$a_1 + a_2 \frac{100}{T-\theta} + a_3 b_2$	0.178374	0.043569	-0.011650			0.014452		
(4-3)	$a_1 + a_2 \frac{100}{T-\theta} + a_3 b_2^2$	0.161244	0.044360	-0.001610			0.015917		
(4-4)	$a_1 + a_2 \frac{100}{T-\theta} + a_3 b_2^{0.5}$	0.208000	0.044021	-0.039138			0.014099		
(4-5)	$a_1 + a_2 \frac{100}{T-\theta} + a_3 b_2^{0.5} + a_4 b_2$	0.214722	0.044228	-0.048472	0.002855		0.014085		
(4-6)	$a_1 + a_2 \frac{100}{T-\theta} + a_3 b_2^{0.5} + a_4 T \cdot 10^{-3}$	0.039434	0.071431	-0.039627	0.428875		0.013534		
(4-7)	$a_1 + a_2 \frac{100}{T-\theta} + a_3 b_2^{0.5} + a_4 T$	0.199758	0.050786	-0.060109	0.065697		0.014029		
	$10^{-3}b_2^{0.5}$								
(4-8)	$a_1 + a_2 \frac{100}{T-\theta} + a_3 b_2^{0.5} + a_4 b_1$	0.207718	0.044159	-0.039162	0.000897		0.014098		
(4-9)	$a_1 + a_2 \frac{100}{T-\theta} + a_3 b_2^{0.5} + a_4 P$	0.207231	0.044558	-0.039267	0.000142		0.014093		
(4-10)	$a_1 + a_2 \frac{100}{T-\theta} + a_3 b_2^{0.5} + a_4 T$	0.038343	0.071471	-0.039595	0.432717	-0.001332	0.013531		
	$10^{-3} + a_5 b_1$								
Second round	of fitting								
(4-10)	$a_1 + a_2 \frac{100}{T-\theta} + a_3 b_2^{0.5} + a_4 T \cdot$	0.113910	0.062720	-0.038667	0.223006	-0.001096	0.008462		
	$10^{-3} + a_5 b_1$								

T: temperature (K), θ = 228 K, *P*: total pressure (MPa).

by approaching equilibrium from only one direction, mostly via dissolution of CO₂ into undersaturated solutions (Table 2). Such non-reversed experiments are not less accurate *per se*, but it is simply more difficult to be confident in their results in retrospect.

The lack of an experimental demonstration of reversibility is somewhat compensated if long equilibration times are allowed at fixed *T*–*P*–*x* conditions prior to measurement of CO₂ solubility. Therefore, equilibration time has been used as a further criterion of data quality. We have accordingly divided the non-reversed studies into two groups: those with long (\geq 3 h) or unstated equilibration times (Harned and Davis [18]; Yasunishi and Yoshida [26]; Vasquez et al. [36]; Zheng et al. [38]) and those with short times (Yeh and Peterson [20]; the high-salinity data in Gerecke [22]; Drummond [28]; Kiepe et al. [7]). Less weight was applied to the latter group (cf. columns 3 and 4 in Table 3).

Drummond [28] used an isoplethic, quasi-isochoric reversal method to study solutions of 1, 2, 4 and 6 molal NaCl. Measurements were made during heating to 400 °C and then during subsequent cooling. However, below 100 °C no cooling data are reported for the 2 and 3 molal NaCl solutions and only sparse cooling data are reported for the 1, 4 and 6 molal solutions. Altogether only about a dozen of the 93 data below 100 °C in the ternary system are actually reversed (or can be treated as reversed following graphical interpolation). Because the solubility of CO₂ decreases along the quasi-isochores up to 100 °C, the heating steps involve CO₂ exsolution from supersaturated solutions, whereas the cooling steps involve CO₂ dissolution into undersaturated solutions. The difference in CO₂ solubility between the heating and cooling steps is large, up to 10% relative. Below 100 °C the values of solubility for the heating steps are consistently higher than those for the cooling steps, in line with the expected exsolution/dissolution kinetics, bearing in mind that only about 7-8 min were allowed for equilibration prior to each measurement. Surprisingly, the experiments between 100 and 400 °C display the same solubility differences, the heating runs yielding higher CO₂ contents than the cooling runs. This is inconsistent with the expected kinetics, since the solubility of CO₂ increases with temperature over this interval. While it is thus clear that the high-temperature data suffer from a strong systematic error, it is not obvious to what extent the low-temperature data are also affected. In addition to these uncertainties, the data show high scatter (low precision). Moreover, we encountered problems in reproducing the reported partial pressures of H₂O, as also noted in Ref. [43]. Therefore, according to our evaluation scheme

the data in Drummond [28] fall into column 4 in Table 3. Owing to the high deviations of the binary measurements (mostly negative deviations up to 11%), the dataset is assigned zero weight.

The study of Cramer [29] acknowledged poor reproducibility $(\pm 3-8\%)$ of the reported CO₂ solubility values and so, despite the long time allowed for equilibration, somewhat lower confidence was assigned by lumping it with the studies in column 4 in Table 3. The data of Koschel [42] were treated in the same way because the authors report a large uncertainty in the derived CO₂ concentrations $(\pm7\%)$. Theirs is the only one of the assembled publications that determined CO₂ solubility from the enthalpy change upon mixing with the NaCl solution.

Only in two cases could purely theoretical criteria be applied to discriminate data quality. The first of these (column 5 in Table 3) concerns the limiting behaviour of the ratio $\ln(b_1^o/b_1)$. This should tend to zero as the concentration of NaCl in solution approaches zero. The data of Gerecke [22] above 35 °C and the data of Kiepe et al. [7] at 80 °C were the only ones not to pass this test and so the measurements at these temperatures were discarded.

The second theoretical criterion relates to the behaviour of the partial molar volume of dissolved CO_2 as a function of pressure (column 6, Table 3). Malinin [32] thoroughly investigated the role of pressure on the salting-out of CO_2 and concluded that, up to 200 °C, the partial molar volume of aqueous CO_2 in salt solutions is equal to that in pure water. A useful relation in this context can be derived (Appendix B) using the Setchenow coefficient defined in Eq. (1):

$$\frac{\partial k_{Sbb}}{\partial P} = \frac{1}{RT} \frac{\Delta \overline{V}_{m,CO_2}}{b_2},\tag{2}$$

where and $\Delta \overline{V}_{m,CO_2}$ is the difference in the partial molar volume of CO₂ dissolved in a solution with NaCl molality of b_2 compared to that in pure water. Hence, setting $\Delta \overline{V}_{m,CO_2}$ equal to zero according to the findings of Malinin [32] implies that k_{Sbb} does not depend on pressure over the temperature range of our study (0–100 °C). In contrast to this conclusion, the experiments of Nighswander et al. [30] reveal a significant dependency of k_{Sbb} on pressure over the interval 4–8 MPa. Insertion of their data into Eq. (2) as follows:

$$\Delta \overline{V}_{m,CO_2} = b_2 RT \frac{\partial k_{Sbb}}{\partial P} = 0.173 \cdot 8.314 \cdot 353 \cdot (-0.032)$$
$$= -16 (\pm 5) \text{ cm}^3 \text{ mol}^{-1},$$

yields a strong decrease in the partial molar volume of CO₂ compared to that in pure water, even though the concentration of NaCl in their experiments, b_2 , was only 0.173 molal. This result also conflicts with the absolute value of the partial molar volume of CO₂ in pure water, $\overline{V}_{m,CO_2^0} \approx 33.4 \text{ cm}^3 \text{ mol}^{-1}$ [45]. Moreover, the data of Rumpf et al. [34] over the same *T*–*P* range but at higher concentrations of NaCl (3–4 molal) do not reveal any dependency on pressure. Likewise, the data of Bando et al. [41] for NaCl concentrations up to 0.56 molal show no pressure effect between 10 and 20 MPa. In view of all this the data of Nighswander et al. [30] were not included in our dataset for fitting.

The Setchenow coefficients of Kiepe et al. [7] also show a strong dependency on pressure, similar to those of Nighswander [30]). Inserting their data for 0.52 molal NaCl at $40 \,^{\circ}$ C into Eq. (2) yields:

$$\Delta \overline{V}_{m,CO_2} = b_2 RT \frac{\partial k_{Sbb}}{\partial P} = 0.52 \cdot 8.314 \cdot 313.4 \cdot (-0.038)$$
$$= -51.4 \,\mathrm{cm}^3 \,\mathrm{mol}^{-1},$$

a value which is clearly unrealistic. Overall, the dataset of Kiepe et al. [7] displays solubility trends as a function of pressure that contradict all the other datasets reviewed. The source of this discrepancy is unknown. However, the experimental approach was similar to that of Drummond [28], in which an autoclave is loaded with a known mass of NaCl solution and excess gas, and the total gas pressure is measured upon heating in a quasi-isochoric fashion. The authors point out that the calculation of aqueous solubility from the measured gas pressure is complicated and that it involves several assumptions. Based on the same arguments as invoked above for the study of Nighswander [30], we have discarded the 40 °C data of Kiepe et al. [7]. Since the 80 °C data were discarded above owing to the unusual limiting behaviour of $\ln(b_1^o/b_1)$, the entire dataset is assigned zero weight.

The study of Bando et al. [41] covers only a small range of salinities (\leq 0.56 molal NaCl) but it is significant in that it is one of only two literature sources with experimental results above 10 MPa (10–20 MPa; the other being Koschel et al. [42]). The measurements were made using a non-reversed experimental method with a relatively long time (3 h) allowed for equilibration. The values show no discrepancies with respect to the theoretical criteria above, and the deviations of the binary data are at most –6%. As the thermodynamic model developed in the present study is intended to predict CO₂ solubility to 100 MPa, we have chosen to reserve the data of Bando et al. [41] to test its predictions, rather than to use them to constrain the model. Had we used the data for fitting, 27 of the 36 data would have been assigned a weight of 0.75, the rest 0.5, according to our scheme in Table 3.

We have not used the publication by Kim et al. [46] because the experiments were made within the stability field of aqueous liquid $+ CO_2$ -clathrate in the absence of a free carbonic fluid.

3.3. Data screening using a solubility model based on the Setchenow coefficient, k_{Sbb}

In this section the weighted solubility data are screened for erroneous values based on an analysis of their Setchenow coefficients. The first step is to find an empirical formulation for k_{Sbb} that fits as closely as possible all the data as a function of T, P and b_2 , taking into account the weights assigned above. Once an appropriate equation is found, outliers in the datasets are screened out by setting a limit to the allowed deviation. In a second round of processing, the remaining set of more reliable data are refitted to the same equation and screened once again.

Because the variable b_2 appears in the denominator of Eq. (1), isothermal plots of k_{Sbb} versus b_2 show very large scatter at $b_2 < 0.5$. This numerical artefact precludes meaningful evaluation of the

datasets with respect to the limiting behaviour of k_{Sbb} , regardless of the precision of the experimental methods employed. Therefore, to avoid any undetectable bias from poor-quality measurements, all the primary data for $b_2 < 0.5$ were excluded from the initial fitting procedure for k_{Sbb} , irrespective of their assigned weights.

Various equations that describe k_{Sbb} as a function of *T*, *P* and b_2 were tested to minimize the absolute mean-square deviation of k_{Sbb} , denoted σ_{abs} :

$$\sigma_{abs} = \left[\frac{\sum_{i} w_i [(k_{Sbb, model, i} - k_{Sbb, exper, i})]^2}{\sum_{i} w_i - 1}\right]^{0.5}.$$
(3)

Table 4 lists the equations (numbered with prefix "4-"), the fitted coefficients and the calculated values of σ_{abs} . The results of these tests are discussed in the following.

Preliminary comparison of the σ_{abs} values obtained using Eq. (4-1) and several alternatives showed that the temperature dependency of k_{Sbb} is steeper than T^{-1} . Of the alternative factors considered, $(T - \Theta)^{-1}$ was found to be the best, in which $\Theta = 228$ K is the so-called singular point of pure supercooled water [47]. Table 4 shows that Eq. (4-2) yields a better fit (lower σ_{abs}) than Eq. (4-1).

As has been noted in numerous studies, Setchenow's [48] salting-out coefficient, k_{Sbb} , exhibits strong dependency on salt concentration. Comparison of σ_{abs} values demonstrates that the available set of experimental data are better described using a square root $b_2^{0.5}$ dependency (Eq. (4-4)) rather than a linear formulation (Eq. (4-2)) or other variants with exponents greater than one (e.g. Eq. (4-3)). This may be because the slope $\partial k_{Sbb}/\partial b_2$ increases at low salt concentrations, a behaviour which would be better captured by the factor $b_2^{0.5}$. More complicated dependencies on b_2 (e.g. Eq. (4-5) and others not shown) do not improve the description. The fit to the k_{Sbb} data is significantly improved by introducing an auxiliary *T*-term (cf. Eqs. (4-6) and (4-4)). It is interesting that introduction of a pure *T*-term (Eq. (4-6) is more effective than assigning a temperature dependency to the salt molality, b_2 (e.g. Eq. (4-7)).

The assumption that k_{Sbb} depends on the concentration of CO₂, b_1 , slightly improves the fit (cf. Eqs. (4-8) and (4-4)).

The possible influence of pressure on k_{Sbb} was tested using Eq. (4-9). It can be seen that inclusion of a *P*-term does not diminish the absolute error (cf. Eqs. (4-4) and (4-9)). This result is consistent with the conclusion of Malinin [32] and with the results of Rumpf et al. [34], as discussed above.

In conclusion, Eq. (4-4) is the best of the low-parametric expressions:

$$k_{Sbb} = a_1 + a_2 \frac{100}{T - \theta} + a_3 b_2^{0.5} = 0.205027 + \frac{4.5454}{T - \theta} - 0.03865 b_2^{0.5}.$$

Some improvement could be achieved by introducing additional dependencies on temperature and CO_2 molality, as done via Eq. (4-10).

After this first round of fitting, all the experimental data with non-zero weights (now including those for $b_2 < 0.5$) were screened with respect to their deviations from the k_{Sbb} model (Eqs. (4-4) and (4-10)). Data with a relative deviation of $2\sigma_{rel} > 12.4\%$ were deemed to have experimental errors and were discarded. Thus, 22 of the 270 data with positive weights were discarded (6 of the 149 data with weight 0.75, 132 of the 33 data with weight 0.5 and 3 of the 27 data with weight 0.25).

The reduced set of k_{Sbb} values was then fitted to Eq. (4-10) once again. The results of this second round of fitting are given in Table 4. Eq. (4-10) with the following coefficients:

$$k_{Sbb} = 0.116791 + \frac{6.0616}{T - \theta} - 0.0394175b_2^{0.5} + 0.227168 \cdot T \cdot 10^{-3} - 0.001971 \cdot b_1,$$
(4)



Fig. 5. Goodness of fit of model Eq. (4–10) in Table 4 (horizontal line at 0%) to the Setchenow coefficients (k_{Sbb}) of all experimental data assigned positive weights. (a) Relative errors as a function of NaCl molality (b_{NaCl}) and fitting weight. (b) Relative errors as a function of temperature and fitting weight.

was found to describe the k_{Sbb} data with an absolute error of 0.85% (at 1 σ confidence level). This value corresponds to a relative error in CO₂ solubility of approximately 2.1% (one standard deviation), or an error of 2.6% (one standard deviation) if all the data with positive weights in Table 1 are taken into account. Fig. 5 illustrates the scatter of the experimental k_{Sbb} values with respect to fitting equation Eq. (4–10), plotted as a function of salinity and temperature.

4. Thermodynamic description of the CO₂-H₂O-NaCl aqueous liquid

The empirical k_{Sbb} model presented above provides an excellent description of the solubility of CO₂ in aqueous NaCl solutions when used in conjunction with a model for the CO₂-H₂O binary. However, it cannot provide the additional thermodynamic properties that are of interest. In the following we use the k_{Sbb} model to develop an appropriate thermodynamic description.

Several different approaches have used to describe gas solubilities in saline solutions. An extensive review of advances up to the early 1980s is given by [49], and more recent progress is reviewed by [50,51]. The models include those based on the cubic EoS formalism with various modifications to account for the influence of ionic interactions (e.g. [49,52–55]. Other models are based on mean spherical approximations (e.g. [8,56]) or on Pitzer's approach (e.g. [1,34,57–60]).

Pitzer's approach has been chosen for the present study because it enables models to be developed that reproduce experimental data within the limits of their uncertainty. When used to interpolate data, as done here, such models generally tend to be more accurate than those based on other approaches. In the present case the choice of Pitzer's approach is especially convenient, because we can adopt the very precise Pitzer-type model presented by Pitzer et al. [12] for the H_2O -NaCl subsystem of our ternary system.

4.1. Pitzer equations

Pitzer's equations for activity coefficients in ternary gas- H_2O -salt systems are presented in Refs. [59,61–62] and are given in Appendix C. Accordingly, the activity coefficient of CO_2 in a strong 1:1 aqueous electrolyte solution is given by

$$\ln \gamma_1 = 2b_1\lambda_{11} + 3b_1^2\tau_{111} + 2b_2B_{12} + 3b_2^2C_{122} + 6b_1b_2C_{112},$$
(5)

where subscript 1 stands for CO_2 and 2 for the electrolyte, while coefficients λ , τ , B, and C indicate the short-range interactions between solvents. For the electrolyte, the mean activity coefficient is

$$\ln \gamma_2 = f^{\gamma} + b_2 B_2^{\gamma} + b_2^2 C_2^{\gamma} + 2b_1 B_{12}^{\varnothing} + 3b_1 b_2 C_{122} + \frac{3}{2} b_1^2 C_{112}.$$
 (6)

Here, $f^{\gamma} = -A_{\varnothing}((I^{0.5}/(1+bI^{0.5})) + (2/b)\ln(1+bI^{0.5}))$, where *I* denotes the ionic strength of the solution (in mol kg⁻¹), A_{\varnothing} is the Debye–Hückel slope for the osmotic coefficient, and b = 1.2. For a binary H₂O–NaCl solution, $I = b_2$. Detailed expressions for the short-range interaction coefficients are given in Appendix C.

The osmotic coefficient is calculated according to:

$$\emptyset = 1 - \frac{1}{M_{w}} \ln \gamma_{w} \frac{1}{\sum m_{i}} = 1 - \frac{1}{M_{w}} \ln \gamma_{w} \frac{1}{(b_{1} + 2b_{2})},$$

which allows the activity of water to be determined from

$$\ln a_w = -\varnothing \cdot M_w \sum m_i = -\varnothing \cdot M_w (b_1 + 2b_2).$$

4.2. Estimation of Pitzer parameters

Pitzer parameters for the H₂O–NaCl subsystem were adopted from the Pitzer et al. EoS [12] without any modification. Parameters for the H₂O–CO₂ subsystem were estimated from In γ_1° values for binary H₂O–CO₂ system calculated with the Diamond–Akinfiev model [11], which are valid at 271 \leq T \leq 373 K, 0 \leq b₁ \leq 2.5 and 0.1 \leq P \leq 100 MPa. The data are described by the expression:

$$\begin{split} \ln \gamma_1^\circ &= (-0.099085 + 0.48977 \cdot 10^{-3} \cdot T - 0.962628 \cdot 10^{-6} \cdot T^2) \cdot b_1, \\ &+ (0.218384 - 1.024319 \cdot 10^{-3} \cdot T + 1.222992 \cdot 10^{-6} \cdot T^2) \\ &\cdot b_1^2. \end{split}$$

Inserting this into Eq. (C.1) and rearranging yields:

$$\lambda_{11} = (-0.0495425) + (0.244885 \cdot 10^{-3}) \cdot T + (-0.481314 \cdot 10^{-6}) \cdot T^2,$$

$$\tau_{111} = (0.0727795) + (-0.34141 \cdot 10^{-3}) \cdot T + (0.407664 \cdot 10^{-6}) \cdot T^2.$$

The CO₂–NaCl interaction parameters were obtained as follows. Under the constraints of the equilibrium: $CO_{2(aq)} \Leftrightarrow CO_{2(gas)}$, at given temperature and constant CO₂ fugacity (f_{CO_2}), it follows that:

$$\ln(b_1\gamma_1) = \ln(b_1^\circ\gamma_1^\circ). \tag{7}$$

Here, as above, b_1 and b_1° are the molalities of $CO_{2(aq)}$ and γ_1 and γ_1° are the activity coefficients of $CO_{2(aq)}$ in the ternary CO_2-H_2O -NaCl and binary CO_2-H_2O systems, respectively. Writing Eq. (7) in this way does not explicitly account for the difference in f_{CO_2} between the NaCl-bearing and the NaCl-free systems, which arises due to the change in solubility of H_2O in the saturating carbonic phase (whether liquid or vapour) as a function of aqueous salinity. Ignoring this effect entirely would result in a mean error in predicted b_1 of around 0.3%. Our model includes this small effect, but, for convenience, we have chosen to incorporate it within γ_1 , via our fits to the experimental database. Thus, the definition of γ_1 used here

Table 5

Equations used to test fit Pitzer parameters by means of the function $F(T, b_2, b_1, I)$.

Fitting equation F		Coefficients	Coefficients							
		<i>a</i> ₁	<i>a</i> ₂	<i>a</i> ₃	<i>a</i> ₄	<i>a</i> ₅	<i>a</i> ₆	$\sigma_{abs(sol)}$		
First round	of fitting									
(5-1)	$a_1 + a_2 \frac{100}{T-\theta} + \frac{3}{2}a_4b_2$	0.080606	0.025153		-0.003193			0.028515		
(5-2)	$a_1 + a_2 \frac{100}{T-\theta} + a_3 T \cdot$	0.045121	0.031441	0.087587	-0.003188			0.028154		
	$10^{-3} + \frac{3}{2}a_4b_2$									
(5-3)	$a_1 + a_2 \frac{100}{T-\theta} + \frac{3}{2}(a_4 +$	0.078985	0.026460	0.002903	-0.004118			0.028504		
	$a_3T \cdot 10^{-3})b_2$									
(5-4)	$a_1 + a_2 \frac{100}{T-\theta} +$	0.079497	0.026053	-0.000206	-0.002543			0.028522		
	$\frac{3}{2}\left(a_4 + a_3 \frac{1000}{T}\right)b_2$									
(5-5)	$a_1 + a_2 \frac{100}{T - \theta} +$	0.083947	0.022408	0.000460	-0.003732			0.028386		
	$\frac{3}{2}\left(a_4+a_3\frac{100}{T-\theta}\right)b_2$									
(5-6)	$a_1 + a_2 \frac{100}{7.6} + \frac{3}{2} a_4 b_2 + \frac{3}$	0.081006	0.024996		-0.003187	-0.000449		0.028459		
	$3a_5b_1$									
(5-7)	$a_1 + a_2 \frac{100}{T-\theta} + a_6 g(x) +$	0.065644	0.025280		-0.002001		0.059990	0.027506		
	$\frac{3}{2}a_4b_2$									
(5-8)	$a_1 + a_2 \frac{100}{T-\theta} + a_6 g(x) +$	0.029338	0.031692	0.089322	-0.001986		0.060460	0.027114		
	$a_3T \cdot 10^{-3} + \frac{3}{2}a_4b_2$									
(5-9)	$a_1 + a_2 \frac{100}{T-\theta} + a_6 g(x) +$	0.029796	0.031563	0.089211	-0.001990	-0.000346	0.060041	0.027075		
	$a_3T \cdot 10^{-3} + \frac{3}{2}a_4b_2 + 2a_4b_1$									
C 1	3a ₅ b ₁									
Second rou	nd of fitting $\pi + \pi = 100$	0.057100	0.026004	0.024000	0.000000	0.000570	0.045.025	0.015070		
(5-9)	$u_1 + u_2 \frac{1}{T-\theta} + d_6 g(x) $	0.057123	0.026994	0.034096	-0.002380	-0.000576	0.045635	0.015878		
	$a_{31} \cdot 10 + \frac{3}{2}a_{4}b_{2} + 3a_{5}b_{1}$									
	54501									

T: temperature (K), θ = 228 K.

implicitly takes account of changes in f_{CO_2} , and hence it departs slightly from conventional definitions.

Rearrangement of Eq. (7) yields the change in solubility of $CO_{2(aq)}$ caused by the presence of the electrolyte:

$$\ln \frac{b_1^\circ}{b_1} = \ln \frac{\gamma_1}{\gamma_1^\circ}.$$
(8)

Now substituting Eqs. (C.1) and (C.2) we obtain:

$$\ln \frac{b_1^{\circ}}{b_1} = \ln \frac{(\gamma_1^{\circ})_{b_1^{\circ}}}{(\gamma_1^{\circ})_{b_1}} + 2b_2B_{12} + 3b_2^2C_{122} + 6b_1b_2C_{112}.$$
 (9)

Eq. (9) was used to estimate binary (B_{12}) and ternary (C_{122}, C_{112}) short-range interaction parameters using the accepted set of 333 experimental $\ln(b_1^{\circ}/b_1)$ values remaining after the preliminary discarding procedure. The first step was to recast Eq. (9) into the form of a fitting function, *F*, which incorporates only the experimentally measured variables. Based on the reasoning presented in the treatment of k_{Sbb} above, a possible dependency of *F* on pressure was ruled out. Thus, the task was reduced to finding an appropriate form of *F* in terms of the variables *T*, b_1 , b_2 , and *I*:

$$\ln \frac{b_1^{\circ}}{b_1} - \ln \frac{(\gamma_1^{\circ})_{b_1}}{(\gamma_1^{\circ})_{b_1}} = 2b_2 \left(B_{12} + \frac{3}{2}b_2C_{122} + 3b_1C_{112} \right)$$
$$= 2b_2F(T, b_2, b_1, I).$$

Numerous expressions describing $F(T, b_2, b_1, I)$ (Table 5; equations prefixed by "5-") were tested in order to find the Pitzer interaction parameters that minimize the deviation of the model solubilities $(b_{1,model})$ from the experimental values $(b_{1,exper})$. Defining the relative deviation of the solubility as:

$$r_{sol} = \frac{b_{1,model} - b_{1,exper}}{b_{1,exper}},\tag{10}$$

the expression that yields the minimum mean deviation was identified by comparing the standard deviation (σ) of r_{sol} values

calculated using each equation in Table 5 in turn, where

0 5

$$\sigma_{r(sol)} = \left[\frac{\sum_{i} w_i (r_{sol,i})^2}{\sum_{i} w_i - 1}\right]^{0.5}.$$
(11)

The standard deviations are listed in the rightmost column in Table 5, and the performance of the tested expressions are discussed in the following.

The preparatory modelling of k_{Sbb} in Section 3.3 demonstrated that the experimental data are best described when the binary interaction parameter, B_{12} , is assigned some form of temperature dependency. Eq. (5-1) provides for such a dependency by means of the terms $B_{12} = a_1 + a_2(100/(T - \theta))$, while the ternary parameter $C_{122} = a_4$ is held independent of temperature. Comparison of the deviations resulting from Eqs. (5-2) and (5-3) shows that allowing for a temperature dependency of C_{122} (Eq. (5-3)) is slightly more favourable than inclusion of an additional temperature-dependent term in B_{12} (Eq. (5-2)). In Eq. (5-3), C_{122} is represented by the term $(3/2)(a_4 + a_3T \ 10^{-3})$. The negative value that arises for a_3 implies that C_{122} diminishes with increasing temperature, whereas the reciprocal dependency (T^{-1}) tested in Eq. (5-4) (where $C_{122} = (3/2)(a_4 + a_3(1000/T))$ results in a positive coefficient and an essentially identical fit.

Incorporation of ternary interaction parameters ($C_{112} = a_5$ in Eq. (5-6)) improves the fit to the data slightly (cf. Eqs. (5-2) and (5-6)), and the very small value of a_5 appears to be physically reasonable.

It is usual to set the binary neutral–ionic interaction parameter B_{12} independent of ionic strength, in contrast to the ion–ion interaction parameter $B_2 = \beta_2^{(0)} + \beta_2^{(1)} \cdot g(\alpha I^{0.5})$. Indeed, Pitzer [61] deliberately pointed out that there is no empirical evidence for an ionic-strength dependence of the λ 's for neutral species. Nevertheless, incorporation into Eq. (5-7) of a dependency analogous to B_2 , such that $B_{12} = \beta_{12}^{(0)} + \beta_{12}^{(1)} \cdot g(\alpha I^{0.5})$, causes a noticeable improvement to the fit (cf. Eqs. (5-7) and (5-1)). In Eq. (5-7) the term $\beta_{12}^{(0)} = a_1 + a_2(100/(T - \theta))$ is assumed to be dependent on tem-



Fig. 6. Goodness of fit of model Eq. (5-9) in Table 5 (horizontal line at 0%) to all the experimental CO₂ solubility data assigned positive weights. (a) Relative errors as a function of NaCl molality (b_{NaCl}) and fitting weight. (b) Relative errors as a function of temperature and fitting weight.

perature whereas $\beta_{12}^{(1)} = a_6$ remains independent. As usual we set $\alpha = 2.0$ and $x \equiv \alpha I^{0.5}$.

The most precise fit of all is given by Eq. (5-9), in which $B_{12} = \beta_{12}^{(0)} + \beta_{12}^{(1)} \cdot g(\alpha I^{0.5})$, $\beta_{12}^{(0)} = a_1 + a_2(100/(T - \theta))$, $\beta_{12}^{(1)} = a_6$, $C_{122} = a_4 + a_3(1000/T)$ and $C_{112} = a_5$. This equation describes the solubility of CO₂ in NaCl solutions with a relative error of 2.7% at 1σ confidence level. Finally, it is interesting to note that Eq. (5-7), a shorter expression with temperature-independent terms $C_{122} = a_4$ and $C_{112} = 0$, yields a relative error of 2.75%, which is only marginally inferior to that of Eq. (5-9).

Based on this first round of fitting the data were filtered again, as done in the fitting of k_{Sbb} above. All experimental data with deviations of $2\sigma_{rel sol} \ge 5.4\%$ with respect to Eq. (5-9) were discarded. The remaining data were run through the fitting procedure again using Eq. (5-9). The results of this second round of fitting are given in the bottom row of Table 5. Thus, of a total of 333 data with positive weights (Table 1), 31 points were discarded. These include 1 datum of the 66 assigned w = 1.00, 3 of the 186 data assigned w = 0.75, and 15 of the 43 data assigned w = 0.5, and 12 data of 38 data assigned w = 0.25.

In conclusion, Eq. (5-9) in Table 5 (second round) describes the retained set of data with a relative error of about 1.6% at the 1σ confidence level. If all the data with positive weights in Table 1 are considered, Eq. (5-9) yields a fit with a 1σ confidence of 2.7%. Fig. 6 displays the fit of Eq. (5-9) to all the data that were assigned positive weights, and Fig. 7 compares the fit to both the accepted and rejected datasets, as a function of temperature and aqueous salinity.

4.3. Molar volume and density of the aqueous $CO_2-H_2O-NaCl$ liquid

Provision has been made in the new model to calculate the molar volume (V_m) and hence density of the bulk ternary solution at any concentration of NaCl and of CO₂ up to saturation. The following approximation is used:

$$V_m = \frac{b_1}{b_1 + b_2 + 55.508} V_{m,1}^{\infty} + \frac{55.508}{b_1 + b_2 + 55.508} V_{m,H_2O} + \frac{b_2 + 55.508}{b_1 + b_2 + 55.508} V_{m, \text{NaCl,aq}},$$
(12)

where $V_{m,1}^{\infty}$ is the partial molar volume of CO₂ at infinite dilution in NaCl-free aqueous solution (cm³ mol⁻¹) obtained from the Akinfiev–Diamond EoS [63], V_{m, H_2O} is the molar volume of pure H₂O computed with the Hill EoS [64] and $V_{m, NaCl, aq}$ is the apparent molar volume of NaCl_(aq) in the CO₂-free, H₂O–NaCl mixture (cm³ mol⁻¹). The latter is calculated from the value of Na⁺Cl⁻_(aq) at infinite dilution given in the HKF model database [65], by applying Pitzer's corrections [12] for the specified molality of NaCl.

4.4. Saturation conditions of solid phases

In order to calculate the stability limits of the aqueous solution with respect to the solid phases in the system, thermodynamic functions for ice, hydrohalite, halite and clathrate have been incorporated into the model.

For the first three phases, equilibrium constants for the dissolution reactions at infinite dilution were calculated from data in ref. [65] over the T-P region of interest and fitted to polynomial functions. The equilibrium constants are solved for finite concentrations using the activity coefficients for the CO₂–H₂O–NaCl system generated by the model in this study.

For CO₂-clathrate, the statistical thermodynamics approach [66–68] has been implemented. Kihara parameters were obtained by fitting experimental data [13,69,70,14], yielding σ = 365 pm and ε/k = 173.44 K. Cage occupancies in the clathrate structure were then fitted to polynomials as a function of *T* and *P* to allow prediction of clathrate saturation at any selected point. The effect of aqueous NaCl on the saturation conditions is calculated from the corresponding activity of H₂O generated by the present model. The fit to selected experimental data for the ternary system [13,70,71,72] was improved with the following empirical correction to the Langmuir constants (*C*) of the large I cavities:

$$C_{Large, corrected} = C_{Large, binary}$$

$$(1 + 0.07773 \cdot b_{\text{NaCl}} \exp(-0.10279 \cdot b_{\text{NaCl}}^2)).$$

5. Results and discussion

The new model based on Eq. (5-9) (Table 5) allows numerous features of the ternary CO_2-H_2O -NaCl system to be predicted. A portrayal of all these features is not possible in the present publication owing to limitations of space. Therefore, the results of selected examples are shown, beginning with the solubility of CO_2 throughout the $T-P-b_{NaCl}$ stability space of the aqueous solution. In the subsequent sections, attention is focussed on the combined effects that dissolved CO_2 and NaCl have on the liquidi of the four solid phases that bound the field of the aqueous solution. Finally, calculations of solution density are illustrated.



Fig. 7. Relative deviation of the experimentally measured solubility of CO_2 reported in 21 literature studies with respect to model Eq. (5–9) of this study (horizontal lines at 0%). The data are grouped according to temperature and plotted as a function of NaCl molality (b_{NaCl}). Left-hand panels (black symbols) show accepted data used to fit the model. Right-hand panels (grey symbols) show discarded data. Dashed curve: model of Duan and Sun [1].

5.1. CO₂ solubility in aqueous NaCl solutions

Fig. 8 shows the solubility of CO₂ in pure water and in 1, 3 and 6 molal aqueous NaCl solutions up to 100°C and 100 MPa, calculated with the new model (Eq. 5-9). The solubility is contoured in units of CO₂ molality. Each contour represents an isoplethic bubble curve of the system in T-P projection. Continuous contours indicate solubilities in T–P regions where aqueous solution is at stable equilibrium in the ternary CO₂-H₂O-NaCl system. The contours are dashed where they pass through metastable regions, i.e. where clathrate, ice, hydrohalite or halite is supersaturated. Thus, the dashed curves represent the solubility of CO₂ only in the metastable states when the respective solids are absent (e.g. owing to kinetic inhibition). The equilibrium solubility of aqueous CO₂ within the stability fields of the solids (not shown in Fig. 8) is generally quite different from the dashed contours. Fig. 9 shows an example for the same conditions as Fig. 8 h. The equilibrium solubilities are shown by continuous curves (blue) within the halite + SCF_{car} liquidus field. Thus, in Fig. 9 the salinity of the aqueous liquid is 6 molal only outside the liquidus field. Within the field the aqueous liquid is saturated in both CO_2 fluid and halite, and therefore its salinity varies with *P* and *T* (cf. Fig. 2).

Overall, the solubility contours in Fig. 8 display rather complicated features within the modelled *T*–*P* range. Where they cross the $L_{aq} + L_{car} + V$ coexistence curve they undergo distinct kinks in their slopes, reflecting the abrupt changes in $\partial f(CO_2)/\partial T$ and $\partial f(CO_2)/\partial P$ at the phase boundary. At elevated pressure below 40 °C and at low salinities (0–1 molal NaCl; Fig. 8a–d) the solubility contours all have steep positive slopes. However, with increasing salinity the contours develop clear pressure minima, visible at high pressure near the clathrate dissociation curve in Fig. 8f (3 molal NaCl), and between about 0 and 35 °C in the halite-oversaturated field in Fig. 8g and h (6 molal NaCl). With increasing temperature above 40 °C each solubility contour passes through a pressure maximum and then follows a negative slope through to 100 °C.

Comparison of the *T*–*P* positions of selected solubility contours as a function of salinity makes evident the strong salting-out of CO_2 by NaCl. Thus, with increasing salinity, increasingly higher pressures are required to reach a given CO_2 concentration at saturation. The contour for 0.75 molal CO_2 at 100 °C is a good example. With no NaCl present this solubility is reached when the solution is under a pressure of about 9 MPa (Fig. 8b). When 1 molal NaCl is in solution, a pressure of about 13 MPa is required to attain the same CO_2 concentration (Fig. 8d). With 3 molal NaCl present the 0.75 contour lies at about 26 MPa (Fig. 8f), whereas with 6 molal NaCl in solution, fully 68 MPa is required to dissolve 0.75 molal CO_2 (Fig. 8h).

5.2. Activity coefficient of aqueous NaCl

The new model permits calculation of the effect that dissolved CO₂ has on the activity coefficient of aqueous NaCl. Fig. 10a demonstrates that the mean ionic activity coefficient of NaCl ($\gamma_{\pm NaCl}$) increases dramatically when the solution is satu-



Fig. 8. *T*-*P* diagrams showing selected contours of CO₂ solubility in aqueous solutions, calculated using model Eq. (5–9) of this study. Each contour represents an isoplethic bubble curve of the system. Continuous contours show solubilities (in CO₂ molality) within the fields of stable aqueous liquid. Dashed contours are metastable extensions into fields supersaturated with respect to the indicated solids. In all plots the contours with values as shown in (a) and (b) are coloured red to help track their displacement through (c) to (h) as a function of salinity. Thick continuous curves are stable isoplethic phase boundaries. Thick dashed curves are metastable extensions. Abbreviations of phase assemblages as in Fig. 1. (a) Detailed plot of CO₂ solubility in the CO₂–H₂O binary subsystem below 50 °C and 10 MPa. (b) Expanded *P*–*T* plot of CO₂ solubility in 1 molal NaCl solution. (d) Expanded *P*–*T* plot of CO₂ solubility in 1 molal NaCl solution. (d) Expanded *P*–*T* plot of CO₂ solubility in 1 molal NaCl solution. (d) expanded *P*–*T* plot of CO₂ solubility in 6 molal NaCl solution. (h) Expanded *P*–*T* plot of CO₂ solubility in 6 molal NaCl solution. (h) Expanded *P*–*T* plot of CO₂ solubility in 6 molal NaCl solution. (h) Expanded *P*–*T* plot of CO₂ solubility in 6 molal NaCl solution. (h) Expanded *P*–*T* plot of CO₂ solubility in 6 molal NaCl solution. (h) Expanded *P*–*T* plot of CO₂ solubility in 6 molal NaCl solution. (h) Expanded *P*–*T* plot of CO₂ solubility in 6 molal NaCl solution. (h) Expanded *P*–*T* plot of CO₂ solubility in 6 molal NaCl solution. (h) ereferences to color in this figure legend, the reader is referred to the web version of the article.)



Fig. 8. (Continued).

rated with CO₂, reflecting the repulsive interactions between the solutes. Fig. 10b shows that, in the presence of dissolved CO₂, the mean ionic activity coefficient of NaCl at infinite dilution is well above 1.0 over the entire temperature range and that it is a strong function of temperature. For the example curve with fixed CO₂ concentration ($b_{CO_2} = 2.0$), the decrease in $\gamma_{\pm NaCl}^{\infty}$ with temperature arises from the fact that the activity coefficient represents $\Delta G^{\text{excess}/RT}$.

5.3. Stability of halite in the CO_2 – H_2O –NaCl system

As the new model provides the activity of aqueous NaCl and as it includes equilibrium constants for halite, the influence of CO₂ on the solubility of halite can be calculated. For an example isotherm at 50 °C, Fig. 11 compares the locus of the solubility boundary (liquidus) in the binary system H₂O–NaCl (according to the EoS of [12]) with that predicted by the new model for the ternary



Fig. 9. *T*–*P* plot equivalent to Fig. 8h with the addition of contours that represent the solubility of CO₂ at stable equilibrium within the halite + SCF_{car} field (continuous blue curves). Aqueous liquid is stable throughout the diagram. In contrast to Fig. 8h, the salinity of the aqueous liquid is 6 molal only outside the halite + SCF_{car} field. Within the liquidus field the salinity varies according to the *T*–*P* conditions (cf. Fig. 2). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

 $CO_2-H_2O-NaCl$ system at saturation with a free carbonic fluid. The predicted curve agrees well with the few available experimental observations [57] (symbols in Fig. 11).

It can be seen that the presence of a carbonic fluid shifts the solubility boundary to appreciably lower aqueous NaCl concentrations, reflecting the increase in $\gamma_{\pm NaCl}$ illustrated in Fig. 10. The same phenomenon is reflected in the *T*–*P* projections in Fig. 8g and h, where saturation in CO₂ stabilizes halite in contact with an aqueous solution of 6 molal NaCl over temperatures between 0.1 and 77 °C (region labelled halite + SCF_{car}). Without CO₂ present (i.e. in the H₂O–NaCl binary), halite is not stable at all in a 6 molal NaCl solution at pressures below 100 MPa [12].

5.4. Stability of ice in the CO_2 -H₂O-NaCl system

Fig. 1 shows the *P*–*T* locus of the quadruple point Q_1 at which ice + CO₂–clathrate + aqueous liquid + vapour are in equilibrium in the binary CO₂–H₂O system. When NaCl is progressively added to the aqueous solution in the ternary, the stability of the Q_1 assemblage shifts to lower temperatures along the quadruple line towards the system eutectic at quintuple point 1. Fig. 12 illustrates the dependency of this temperature shift on salinity, calculated with the new model. The stability of the assemblage ice + aqueous liquid + vapour in the CO₂-free, binary H₂O–NaCl subsystem is shown for comparison. The presence of CO₂ lowers the activity of H₂O and therefore depresses the ice stability field. The relative depression in temperature is quite constant, varying from 1.1° to 1.8°.

5.5. Stability of CO₂-clathrate in the CO₂-H₂O-NaCl system

Similarly to the behaviour of ice, the stability of clathrate is also highly sensitive to the concentration of aqueous NaCl. For example, with increasing salinity the Q_2 assemblage (clathrate + aqueous liquid + carbonic liquid + carbonic vapour) is displaced down the quadruple line to quintuple point 2, located on the solidus (Fig. 1). Model calculations in Fig. 13 illustrate quantitative shifts in Q_2 and in the associated triple curves that delimit the stability of clathrate at low temperatures. A selection of experimental studies, which we judge to be mutually consistent, is shown in Fig. 13 for comparison. The agreement of the model with the experimental data is good over the entire salinity range, although the predicted quintuple point 2 lies about 0.7 °C higher than the value reported in refs. [13,71]. The progressive depression of the clathrate dissociation curve with increasing salinity is also evident in Fig. 8a–f.



Fig. 10. Illustration of the influence of dissolved CO₂ on the thermodynamic properties of aqueous NaCl. (a) Change in the mean ionic activity coefficient of NaCl ($\gamma_{\pm NaCl}$) owing to the presence of CO₂ in solution, at fixed *T* (16 °C) and *P* (100 MPa). Curve with CO₂ is calculated for equilibrium with carbonic liquid. (b) Isobaric (*P*=100 MPa) variation of the mean ionic activity coefficient of NaCl at *infinite dilution* ($\gamma_{\pm NaCl}^{\infty}$) as a function of temperature. Upper curve is for CO₂ concentration at saturation with respect to CO₂. Lower curve is for a fixed molality of aqueous CO₂ ($b_{CO_2} = 2$). Dashed segments lie in the metastable region of clathrate supersaturation. In the absence of dissolved CO₂ the plotted curve would be equal to 1.

5.6. Stability limits of CO₂-saturated aqueous liquid at low temperatures

Counting T, P, V_m (or density) and the two compositional variables (b_{NaCl} , b_{CO_2}), the phase relations in the CO₂-H₂O-NaCl system can be viewed in 10 different two-dimensional diagrams. Figs. 1



Fig. 11. Pressure–salinity plot at 50 °C of the CO₂-saturated halite liquidus in the ternary CO₂–H₂O–NaCl system (continuous curve) and of the halite liquidus in the binary H₂O–NaCl system (dot–dash curve). Both curves are calculated using the model in this study. Dots with error bars are experimental data from Ref. [57]. SCF_{car}: supercritical carbonic fluid.

and 2 show two of these views (T-P and $T-b_{NaCl}$). To provide additional insight into the system, Fig. 14 displays the positions of the various liquidi (solubility limits) in the compositional space $b_{NaCl} - b_{CO_2}$. The calculations have been made for the same four polythermal isobars as illustrated in Fig. 2 (the traces of the isobars at 0.1, 0.9 and 4MPa are also indicated in Fig. 1). It can be seen that increasing the aqueous salinity reduces the isobaric CO₂ solubility along the liquidi under conditions of CO₂ saturation, except at high pressures along the halite liquidus (e.g. 100 MPa curve).



Fig. 12. Polybaric, $b_{NaCI}-T$ projection of the CO₂-saturated Q₁ phase assemblage in the CO₂-H₂O-NaCl system (continuous curve) compared to the ice liquidus in the H₂O-NaCl binary system (dot-dash curve), calculated with the model in this study. Open dot: ternary system eutectic. Solid dot: binary eutectic. The depression of the thermal stability limit of ice as a function of NaCl molality is roughly parallel in the two systems, offset by 1.1–1.8 °C.



Fig. 13. *T*–*P* plot of shifts in the CO₂-saturated liquidi of clathrate and ice as a function of aqueous salinity (in mass% NaCl). Predictions of the model in this study (curves) are compared to data from experimental studies [13,14,69–72]. Quintuple points 1 (system eutectic) and 2 (intersection between $L_{aq}L_{car}V$ curve and system solidus) are as indicated in Fig. 1.

5.7. Molar volume and density of the aqueous $CO_2-H_2O-NaCl$ liquid

The equation used in the model to calculate the bulk molar volume of the aqueous liquid (Eq. (12)) is an approximation and it is



Fig. 14. Stability limits of CO₂-saturated aqueous liquid in the low temperature portion of the CO₂-H₂O-NaCl system. Curves are polythermal, isobaric liquidi (saturation boundaries) of the 4 solids in the system. The same liquidi are visible in *T*-salinity projection in Fig. 2. The isobars illustrate the range in phase relations that occur within the system up to 100 MPa. Three of the isobars are marked in Fig. 1 to aid understanding. Dots are quadruple points: Q₁, Q₂, isobaric eutectics (E) and peritectics (P). Colours of quadruple points correspond to colours of curves in Fig. 1. It can be seen that increasing the aqueous salinity reduces the isobaric CO₂ solubility except at high pressures along the halite liquidus (e.g. 100 MPa curve). All features are calculated using the model in this study.



Fig. 15. Comparison of the densities of $CO_2-H_2O-NaCl$ aqueous liquid predicted by the model in this study (continuous curves) and by the EoS of Duan et al. [4] (dashed curves). Three isobars are shown with aqueous salinity held constant at 3 molal NaCl. To facilitate direct comparison, the curves are calculated for fixed CO_2 concentrations slightly below saturation in each model.

therefore likely to lose accuracy at high CO₂ concentrations and at high *T*–*P* conditions. In an exact formulation $V_{m,1}^{\infty}$ would be substituted by $V_{m,1}$, the apparent partial molar volume of CO₂ in solution. Unfortunately, we have been unable to find reliable experimental volumetric data for ternary mixtures in the *P*–*T* region of interest, and so values of $V_{m,1}$ have not been derived. The only study we are aware of is [30], but it reports measurements just for 0.17 molal NaCl at CO₂ saturation, and in Section 3.2 above it was demonstrated that the values suffer from systematic errors.

In the absence of suitable experimental data to test the model predictions, Fig. 15 compares the densities calculated with the new model to those generated by the EoS of Duan et al. [4]. Three isobars at 1, 10 and 100 MPa are illustrated, all with salinity held constant at 3 molal. To avoid the effects of differences in predicted CO₂ solubilities between the models, the isobars have been calculated for fixed CO₂ concentrations slightly below the respective saturation values. The results diverge appreciably at high pressures. Like the present model, the EoS of Duan et al. [4] is not based on a fit to ternary density data, and so its predictions largely reflect the choice of models used for the binary subsystems and for mixing in the ternary. Duan et al. [4] use the Rogers-Pitzer [73] model for densities of the H₂O-NaCl binary. The present study uses the identical basis incorporated in the formulation by Pitzer et al. [12]. Predictions of the densities of H₂O-NaCl binary mixtures are accordingly indistinguishable. The differences between the models must therefore lie in the values and treatment (e.g. Eq. (12)) of the partial molar volume of CO₂. Duan et al. [4] derived apparent partial molar volumes of CO₂ from experimental data on binary CO₂-H₂O mixtures [45,74–76] and on a multi-electrolyte brine [71]. The present model incorporates values from the Akinfiev-Diamond EoS [63], which includes rigorous provision for the effects of pressure.

6. Conclusions

6.1. Accuracy of the CO₂ solubility model

Up to 10 MPa the new model (Eq. (5-9) in Table 5) fits the accepted experimental data on CO₂ solubility with good precision (1.6% at the 1σ confidence level). This rather small deviation shows



Fig. 16. Comparison of predictions of the model in this study (horizontal line at 0%) with selected experimental data on CO_2 solubilities at and above 10 MPa. The measurements of Koschel et al. [42] are the only data used to constrain the model above 10 MPa. The data of Bando et al. [41], which were not used in the fitting, display relative deviations that are independent of pressure.

that there are no serious inconsistencies among the retained data. However, the accuracy of the model still depends on the extent to which our evaluation and weighting of the experimental database is valid. For example, we justified discarding the large dataset of Drummond [28], but had we retained it in our fitting procedure (as done in the Duan–Sun model [1]) and assigned heavy weights, both the results and the nominal precision of our model would have been significantly different. Thus, the differences in predicted CO₂ solubilities between our model and those of other workers (e.g. [1]; Fig. 7), are largely explained by the choice of data used as fitting constraints, rather than by the thermodynamic formulations adopted.

Only 6 of the 302 ternary experimental data used to constrain the new model are valid for pressures above 10 MPa, the maximum being 20 MPa (Fig. 3). Therefore, although the model is well anchored by the binary subsystems up to 100 MPa ([12] for $H_2O-NaCl$; [11] for CO_2-H_2O), the CO_2 solubilities and other properties calculated by the model are pure predictions at P>20 MPa. One of the two literature studies with data for pressures between 10 and 20 MPa [41] was reserved to test the accuracy of the model. The dataset is not ideal for this purpose, because only salinities up to 0.56 molal NaCl were investigated, and because the reported solubilities are consistently lower than the model values within the high accuracy region of the model at P < 10 MPa. Nevertheless, the data show approximately the same deviation from the model irrespective of pressure (Fig. 16), indicating that the predictions are at least consistent with the trends of the experimental data at high pressure. Clearly, it would be desirable to have new experiments conducted at high pressures and at higher salinities to test the model predictions more rigorously.

The new model is applicable to temperatures well below the 0° C lower limit of the experiments upon which it is based. The predictions are likely to be fairly accurate down to -22° C for several reasons. First, the Pitzer et al. EoS [12], which is used to describe the binary H₂O–NaCl subsystem in our model, is known to extrapolate well to about -20° C [77]. Second, the Diamond–Akinfiev model [11], which is used in the present model



Fig. 17. *P*–*T* coverage of the model presented in this study. See Fig. 1 for explanation of phase boundaries. The model is applicable only in the unshaded region of the *P*–*T* diagram, within the salinity range where aqueous liquid is stable. The accuracy of the model is high within the box with thick outlines and fair within the dashed region. Outside these regions the accuracy has not been tested.

to describe the binary CO_2-H_2O subsystem, is in turn based on the Span–Wager EoS for unary CO_2 [15] and on the Hill EoS for unary H_2O [64]. Both equations extrapolate reliably to temperatures below 0°C. Consequently, the Diamond–Akinfiev model is also likely to be reliable down to approximately –22 °C. Finally, the fair agreement between the model predictions and the experimental data on low-*T* clathrate stability (Fig. 13) support this conclusion.

In summary, the model predictions between P=0.1 to 10 MPa and T=0 to 100 °C are considered to be highly accurate for the entire salinity range. At pressures up to 20 MPa and at temperatures down to -22 °C, the accuracy has been only partly tested but it appears to be fair. Outside these two T-P regions the accuracy of the new model is essentially unknown (Fig. 17).

6.2. Capabilities of the new model

The model presented in this study provides a thermodynamically consistent description of numerous properties of the aqueous liquid in the ternary $CO_2-H_2O-NaCl$ system. These properties include the activity coefficients and partial molar volumes of $CO_{2(aq)}$, $Na^+Cl^-_{(aq)}$, the activity coefficient and osmotic coefficient of the solvent H_2O , the Setchenow coefficient, and the molar volume, excess molar volume and density of the bulk liquid. The properties can be calculated for any CO_2 concentration up to saturation, and for any NaCl concentration (whether stable or metastable).

In addition to fluid properties, the model calculates the saturation states of the four solid phases that delimit the stability of the aqueous liquid. Thus, liquidus curves for ice, hydrohalite, halite and CO_2 -clathrate-hydrate can all be calculated at any CO_2 concentration up to saturation.

The new model can be obtained in the form of a computer code by contacting the authors or by downloading from the website <*www.geo.unibe.ch/diamond*>.

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Appendix A. Appendix A

The following is the method used to recast an Ostwald coefficient, *L*, into units of molality, in the case where the coefficient is originally reported with respect to a non-standard basis of volume of solution, rather than volume of pure solvent:

$$L = \frac{V_{gas}}{V_{solution}} = \frac{V_{gas}}{V_{H_2O-NaCl} + V_{CO_2^o}b_1}$$
$$= \frac{n_{CO_2} \ [mol] \cdot V_{m,CO_2} \ [cm^3 \ mol^{-1}]}{V_{sol}}$$

Normalising to 1 kg of solvent H_2O , the above expression is equal to:

$$\frac{b_1 \cdot V_{m,CO_2} \,[\mathrm{cm}^3 \,\mathrm{mol}^{-1}]}{V_{\mathrm{H}_2\mathrm{O}-\mathrm{NaCl}} + V_{\mathrm{CO}_2} b_1},$$

where

$$V_{\text{H}_2\text{O}-\text{NaCl}} + V_{\text{CO}_2^0} b_1 = V_{sol} \Big|_{\text{H}_2\text{O}=1 \text{ kg}}.$$

Since

$$\rho_{\rm H_2O-NaCl} = \frac{1000 + b_2 58.443}{V_{\rm H_2O-NaCl}},$$

the molality can be obtained as follows:

$$b_1 = \frac{L \cdot (10^3 + b_2 \cdot 58.443)}{\rho_{\text{H}_2\text{O}-\text{NaCl}}(V_{m,\text{CO}_2} - LV_{\text{CO}_2})}.$$

Appendix B. Appendix B

Eq. (2) is derived as follows. Under the constraints of equilibrium, the reaction: $CO_{2(aq)} \Leftrightarrow CO_{2(g)}$,

implies that:

$$\mu_{aa}^{o}(P, T, b_2) + RT \ln b_1 = \mu_{g}^{o}(T) + RT \ln f_1,$$

where as elsewhere in this study, subscript 1 refers to component CO_2 and subscript 2 to component NaCl. Differentiating with respect to *P* we obtain:

$$RT \frac{\partial \ln b_1}{\partial P} = \frac{\partial}{\partial P} (\mu_g^o(T) + RT \ln f_1 - \mu_{aq}^o(P, T, b_2))$$
$$= V_g(P, T) - V_{aq}(P, T).$$

Comparison of the salt-free $(b_1^0, b_2 = 0)$ and the salt-bearing (b_1, b_2) systems at the same *T* and fugacity of CO₂ yields:

$$RT\frac{\partial}{\partial P}\left(\ln\frac{b_1^o}{b_1}\right) = V_{aq}(b_2) - V_{aq}(b_2 = 0) = \Delta V.$$

Since by definition:

 $k_{sbb} \equiv \frac{1}{b_2} \ln \frac{b_1^o}{b_1},$

we obtain

$$\frac{\partial k_{sbb}}{\partial P} = \frac{1}{RT} \frac{\Delta \overline{V}_{m,CO_2}}{b_2},\tag{2}$$

where *P* is in MPa, $R = 8.31441 \text{ cm}^3 \text{ MPa} \text{ K}^{-1} \text{ mol}^{-1}$, and $\Delta \bar{V}_{m,CO_2}$ (cm³ mol⁻¹) is the difference in the partial molar volume of CO₂ dissolved in a solution with NaCl molality of b_2 compared to that in pure water.

Appendix C. Appendix C

The basic relations for Pitzer's approach are as follows. The activity coefficient of CO₂ in a strong 1:1 aqueous electrolyte solution is given by

$$\ln \gamma_1 = 2b_1\lambda_{11} + 3b_1^2\tau_{111} + 2b_2(\lambda_{1c} + \lambda_{1a}) + 3b_2^2(\tau_{1cc} + 2\tau_{1ca} + \tau_{1aa}) + 3b_1b_2(2\tau_{11c} + 2\tau_{11a})$$

where subscript 1 stands for $CO_{2(aq)}$, subscript 2 stands for $Na^+Cl^-_{(aq)}$, c stands for cation, and a for anion. Symbols λ and τ denote binary and ternary short-range interactions, respectively. To simplify the notation we define

$$B_{12} = (\lambda_{1c} + \lambda_{1a})$$

$$C_{112} \equiv (\tau_{11c} + \tau_{11a})$$

and

$$C_{122} \equiv (\tau_{1cc} + 2\tau_{1ca} + \tau_{1aa}).$$

Then, assuming in the binary H_2O-CO_2 system (denoted by superscript^o in the *b* notation) that:

$$\ln \gamma_1^0 = 2b_1^0 \lambda_{11} + 3(b_1^0)^2 \tau_{111}, \tag{C.1}$$

we obtain

$$\ln \gamma_1 \approx \ln \gamma_1^\circ + 2b_2 B_{12} + 3b_2^2 C_{122} + 6b_1 b_2 C_{112}. \tag{C.2}$$

Eq. (C.2) is nevertheless only approximate because in the ternary system the value of b_1 is less than in the binary, i.e. $b_1 < b_1^0$. The exact expression is

$$\ln \gamma_1 = 2b_1\lambda_{11} + 3b_1^2\tau_{111} + 2b_2B_{12} + 3b_2^2C_{122} + 6b_1b_2C_{112}.$$
 (C.3)

For the electrolyte, the mean activity coefficient is

$$\ln \gamma_{2} = f^{\gamma} + b_{2} \left[\lambda_{cc} + 2\lambda_{ca} + \lambda_{aa} + \frac{1}{2}I(\lambda_{cc}^{'} + 2\lambda_{ca}^{'} + \lambda_{aa}^{'}) \right] \\ + \frac{3}{2}b_{2}^{2}(3\tau_{cca} + 3\tau_{caa}) + b_{1} \left[\lambda_{1c} + \lambda_{1a} + I(\lambda_{1c}^{'} + \lambda_{1a}^{'}) \right] \\ + 3b_{1}b_{2}(\tau_{1cc} + 2\tau_{1ca} + \tau_{1aa}) + \frac{3}{2}b_{1}^{2}(\tau_{11c} + \tau_{11a}).$$
(C.4)

Here, as usual, *I* denotes the ionic strength of the solution (in $mol kg^{-1}$), the prime symbol (') denotes a derivative and:

$$f^{\gamma} = -A_{\varnothing} \left(\frac{I^{0.5}}{1 + bI^{0.5}} + \frac{2}{b} \ln(1 + bI^{0.5}) \right), \tag{C.5}$$

where A_{\varnothing} is the Debye–Hückel slope for the osmotic coefficient, and b = 1.2. For a binary H₂O–NaCl solution, $I = b_2$.

The first three right-hand terms in Eq. (C.4) designate the mean ionic activity coefficient of NaCl in the binary NaCl-H₂O, ln γ_2^{o} . Thus, introducing symbols that are conventional in the framework of Pitzer's approach:

$$\begin{split} B_2 &\equiv \frac{1}{2} (\lambda_{cc} + 2\lambda_{ca} + \lambda_{aa}), \\ B_2^{\varnothing} &\equiv B_2 + IB_2^{'} = \frac{1}{2} \left[\lambda_{cc} + 2\lambda_{ca} + \lambda_{aa} + I(\lambda_{cc}^{'} + 2\lambda_{ca}^{'} + \lambda_{aa}^{'}) \right], \\ B_2^{\gamma} &\equiv B_2 + B_2^{\varnothing}, \\ C_2 &\equiv \frac{1}{2} (3\tau_{cca} + 3\tau_{caa}), \\ C_2^{\varnothing} &\equiv 2C_2 = (3\tau_{cca} + 3\tau_{caa}), \end{split}$$

$$C_2^{\gamma} \equiv 3C_2 = \frac{3}{2}C_2^{\varnothing} = \frac{3}{2}(3\tau_{cca} + 3\tau_{caa}),$$

and assuming the conventional ionic strength dependence of B_2 :

$$B_2 = \beta_2^{(0)} + \beta_2^{(1)} \cdot g(\alpha I^{0.5}),$$

we have

 $B_2^{\varnothing} = \beta_2^{(0)} + \beta_2^{(1)} \exp[-\alpha I^{0.5}],$

$$\ln \gamma_2^{\circ} = f^{\gamma} + b_2 B_2^{\gamma} + b_2^2 C_2^{\gamma}. \tag{C.6}$$

where $g(x) \equiv (2/x^2)[1 - (1 + x)\exp(-x)]$, and $\alpha = 2.0$. Incorporating the analogous designations for interactions between dissolved gas and ions:

$$B_{12}^{\alpha} \equiv \frac{1}{2} [\lambda_{1c} + \lambda_{1a} + I(\lambda_{1c}^{'} + \lambda_{1a}^{'})] = \beta_{12}^{(0)} + \beta_{12}^{(1)} \exp(-\alpha I^{0.5}),$$

we can rewrite Eq. (C.4) in more simple form:

$$\ln \gamma_2 = \ln \gamma_2^\circ + 2b_1 B_{12}^{\varnothing} + 3b_1 b_2 C_{122} + \frac{3}{2} b_1^2 C_{112}$$
$$= f^{\gamma} + b_2 B_2^{\gamma} + b_2^2 C_2^{\gamma} + 2b_1 B_{12}^{\varnothing} + 3b_1 b_2 C_{122} + \frac{3}{2} b_1^2 C_{112}. \quad (C.7)$$

For the activity coefficient of water we then have:

$$-\frac{1}{M_{w}} \ln \gamma_{w} = 2f^{\varnothing}I + b_{1}^{2}\lambda_{11} + 4b_{1}b_{2}B_{12}^{\varnothing} + 2b_{2}^{2}B_{2}^{\varnothing} + 6b_{1}^{2}b_{2}C_{112} + 6b_{1}b_{2}^{2}C_{122} + 2C_{2}^{\varnothing}b_{2}^{3}.$$
(C.8)

Here

$$f^{\varnothing} = -\frac{A_{\varnothing}I^{0.5}}{1 + bI^{0.5}},\tag{C.9}$$

and $M_w = 18.0153 \times 10^{-3} \text{ kg mol}^{-1}$ is the molar mass of H₂O.

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