Modeling of CO_2 Solubility in Single and Mixed Electrolyte Solutions Using the Statistical Associating Fluid Theory

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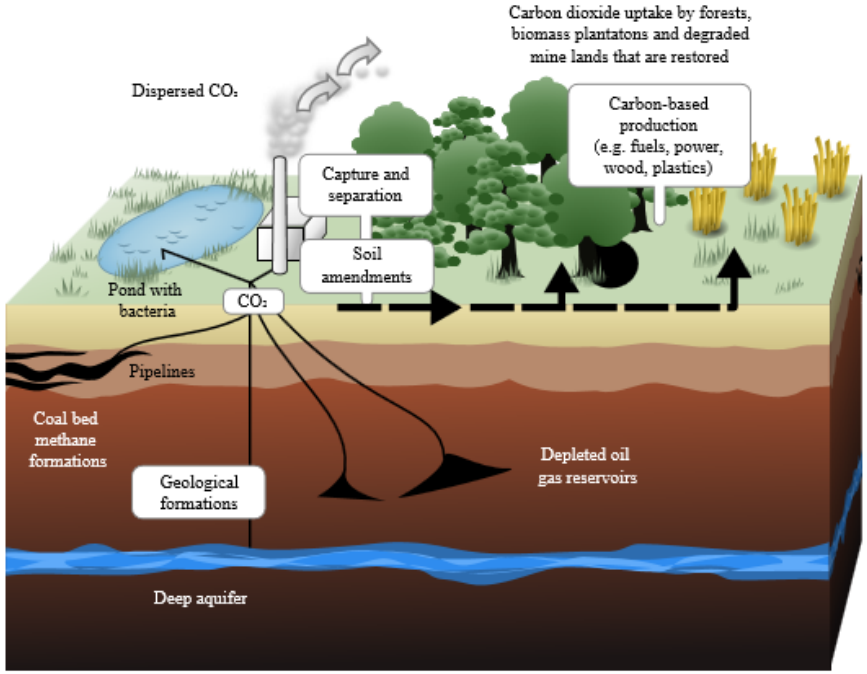
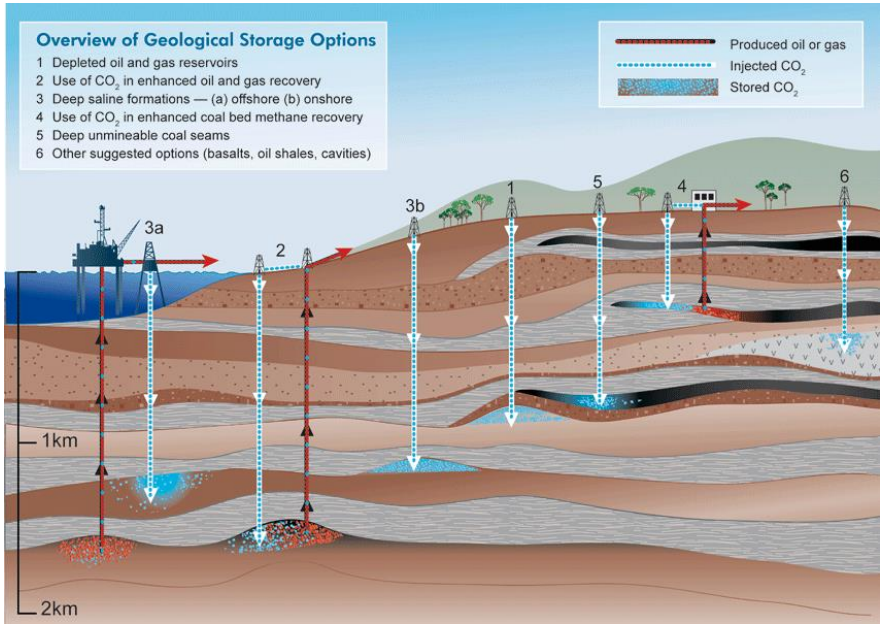
Thermodynamic and Transport Properties of CO_2 – Brine Mixtures are Important for CCS Process Design

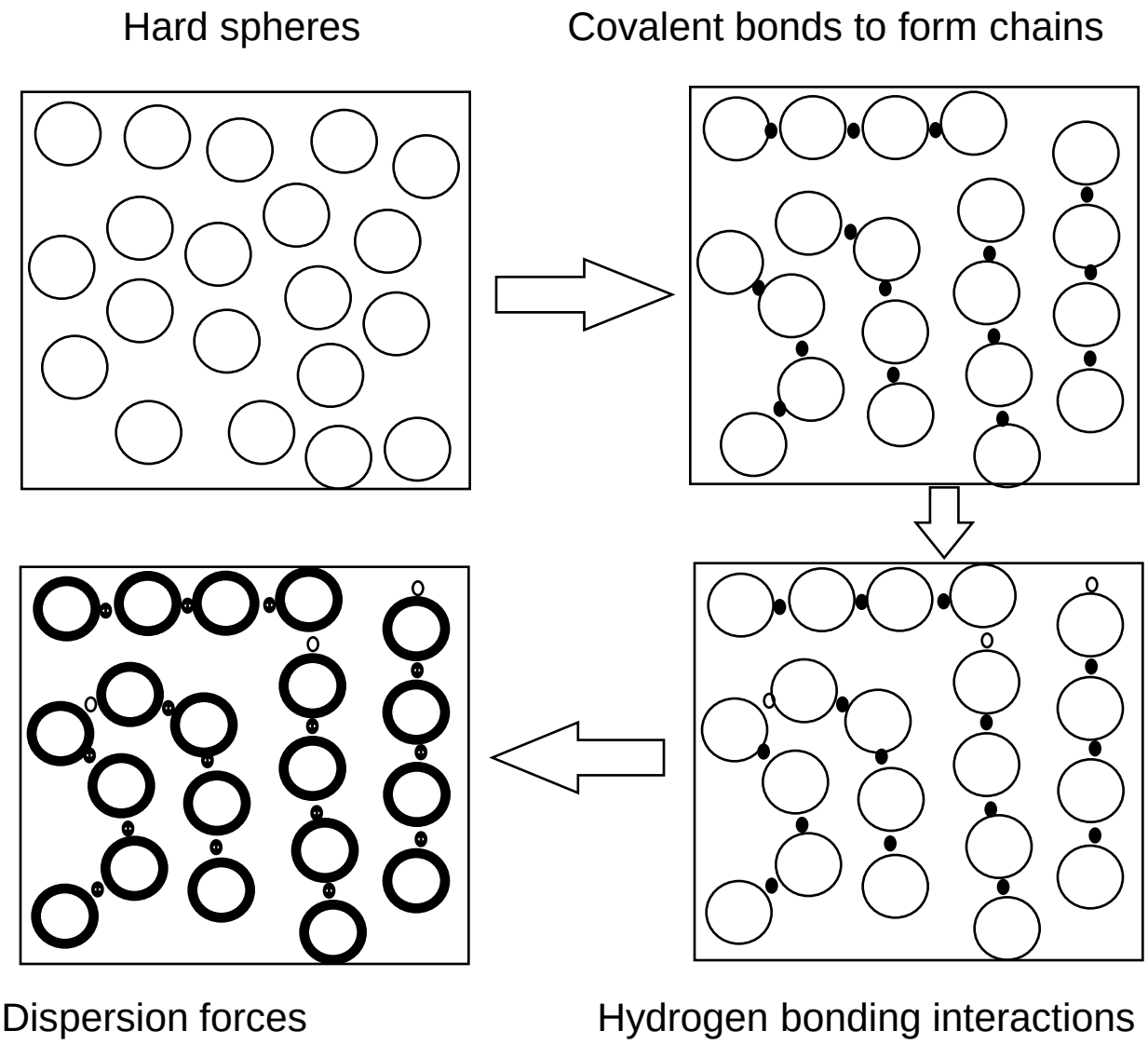




Thermodynamic models for electrolyte solutions

- Debye – Hückel model:
  - Good for infinite dilution only.
- Activity coefficient models, i.e., Pitzer model, NRTL-SAC:
  - Multiple parameters need to be adjusted,
  - Limited predictive power.
- Cubic + Coulombic term:
  - Multiple parameters need to be adjusted.
- Higher order equations of state:
  - Strong theoretical basis,
  - Can be extended to mixtures without further parameter adjustment.

SAFT family of models



(a) Chapman, Gubbins, Jackson, Radosz, *Ind. Eng. Chem. Res.*, 29, 1709 (1990).

(b) Gross, Sadowski, *Ind. Eng. Chem. Res.*, 40, 1244 (2001).

(c) Karakatsani, Spyriouni, Economou, *AIChE J.*, 51, 2328 (2005).

Development of SAFT models

Model	Year	Major development	Authors
TPT1	1988	Wertheim theory is formulated into an EoS for simple fluids	Jackson, Chapman, Gubbins
SAFT	1990	The model is applied to real components – An engineering EoS is formulated	Chapman, Gubbins, Jackson, Radosz
CPA	1996	A cubic EoS is used together with Wertheim formulation for association	Kontogeorgis, Voutsas, Yakoumis, Tassios
SAFT-VR	1997	An attractive potential of variable range is introduced	Gil-Villegas, Galindo, Whitehead, Mills, Jackson, Burgess
Soft-SAFT	1998	The Lennard-Jones reference fluid is introduced	Blas, Vega
SAFT-VRE	1999	Explicit electrostatic interactions are introduced in SAFT-VR	Galindo, Gil-Villegas, Jackson, Burgess
PC-SAFT	2001	A more realistic chain fluid is used as reference	Gross and Sadowski
Polar-SAFT	2001	Explicit polar interactions are introduced	Jog, Sauer, Blaesing, Chapman
ePC-SAFT	2005	Explicit electrostatic interactions are introduced in PC-SAFT	Cameretti, Sadowski, Mollerup
SAFT-VR Mie	2013	A generalized Lennard-Jones potential is used in SAFT-VR	Lafitte, Apostolakou, Avendaño, Galindo, Adjiman, Müller, Jackson

SAFT2-KMSA EoS for H_2O – CO_2 – salt mixtures

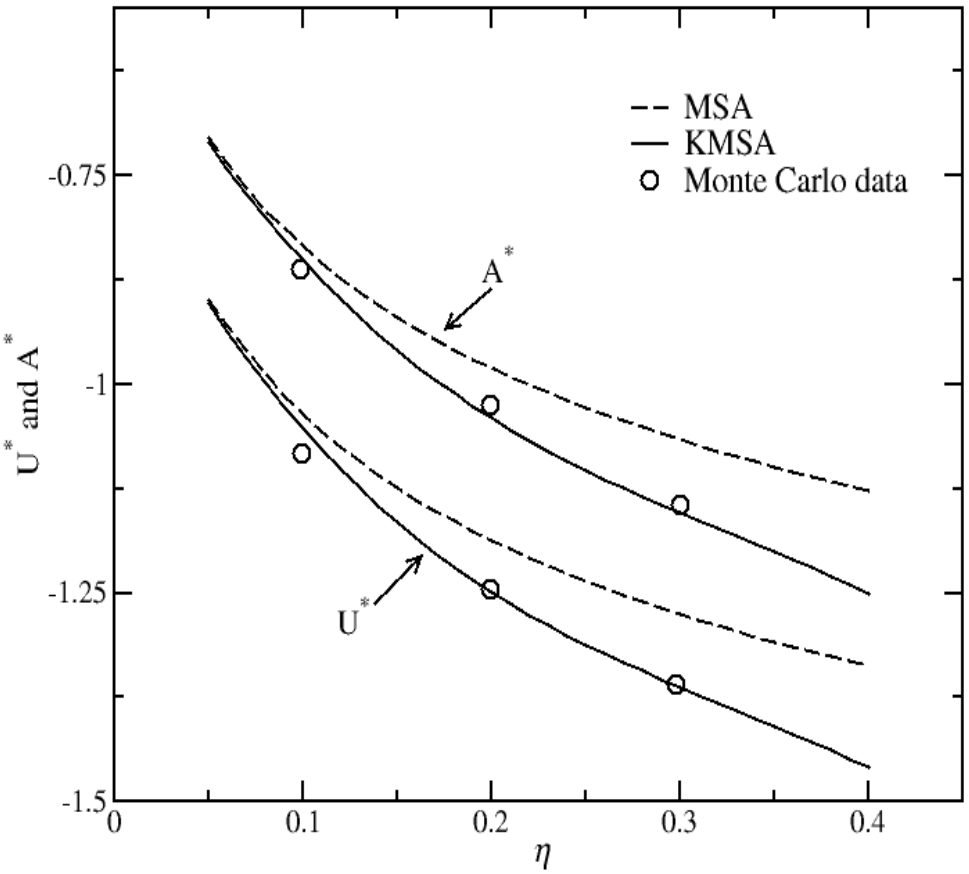
$$\frac{a^{res}(T,\rho)}{RT} = \frac{a(T,\rho)}{RT} - \frac{a^{ideal}(T,\rho)}{RT}$$
$$= \frac{a^{hs}(T,\rho)}{RT} + \frac{a^{disp}(T,\rho)}{RT} + \frac{a^{chain}(T,\rho)}{RT} + \frac{a^{assoc}(T,\rho)}{RT} + \frac{a^{ion}(T,\rho)}{RT}$$

- **Hard sphere term**: Carnahan – Starling EoS, generalized by Mansoori et al. for mixtures.
- **Dispersion term**: 1st order perturbation + Alder et al. polynomial for square well potential.
- **Chain term**: Wertheim theory.
- **Association term**: Wertheim theory.
- **Ion term**: Modified Mean Spherical Approximation (KMSA).

Adidharma and Radosz, *Ind. Eng. Chem. Res.*, 37, 4453 (1998)
Tan *et al., J. Phys. Chem. B,* 110, 16694 (2006)

Modified Mean Spherical Approximation

Ion term: excess Helmholtz energy for RPM system



$$U^* = -\frac{e^2}{4\pi\varepsilon\varepsilon_0 k_B T \sum_i \rho_i}\left\{\Gamma\sum_i \frac{\rho_i z_i^{\,2}}{1+\Gamma K\sigma_i} + \frac{\pi}{2\Delta}\Omega P_n^2\right\}$$

$$A^* = U^* + \frac{\Gamma^3}{3\cdot\pi\cdot\sum_i \rho_i}$$

$$P_n = \frac{1}{\Omega}\sum_i \frac{\rho_i\sigma_i z_i}{1+\Gamma\sigma_i} \qquad \Omega = 1+\frac{\pi}{2\Delta}\sum_i \frac{\rho_i\sigma_i^{\,3}}{1+\Gamma\sigma_i}$$

$$K = 1 - 0.5786\times h + 0.4825\times h^2$$

$$2\Gamma = \left\{\frac{e^2}{\varepsilon\varepsilon_0 k_B T}\cdot\sum_i \rho_i\left[\frac{z_i - (\pi/2\Delta)\sigma_i^{\,2}P_n}{1+\Gamma\sigma_i}\right]^2\right\}^{0.5}$$

Jiang and Adidharma, *Mol. Sim.*, 41, 727 (2015)

CO_2 and ion parameters for SAFT2-KMSA

Species	v (cm^3/mol)	u/k_B (K)	λ/σ	d (Å)
CO_2	7.593	167.188	1.565	-
Na^+	0.200	2036.454	1.659	4.235
K^+	0.205	2422.713	1.978	4.689
Ca^{2+}	0.334	1489.515	2.210	4.455
Mg^{2+}	0.203	1086.357	2.016	5.011
Cl^-	T-dependent	2447.784	1.973	5.429
SO_4^{2-}	T-dependent	1695.242	1.435	3.516
Br^-	T-dependent	2262.856	2.135	5.788

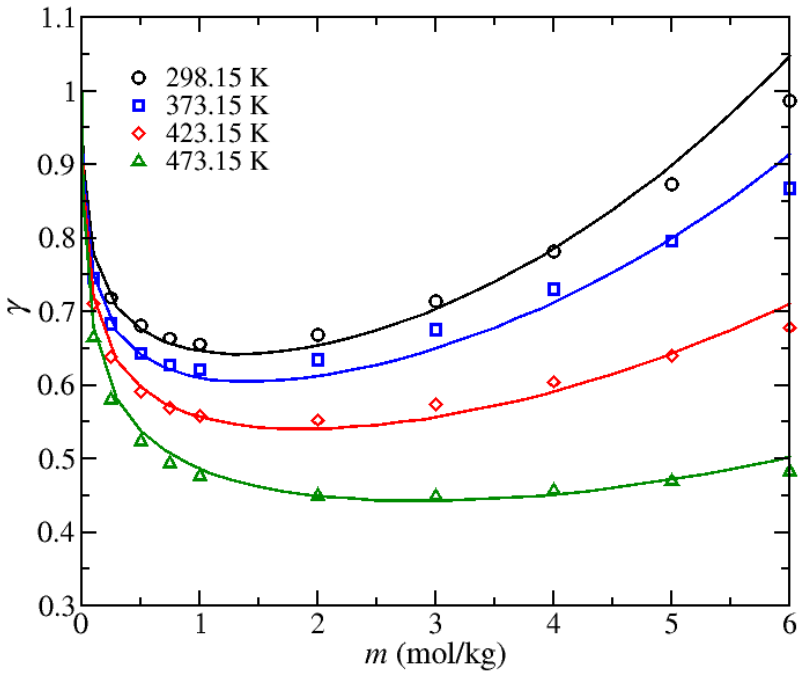
For anions: $v = b_0 + b_1 \times (T - 298.15) + b_2 (T - 298.15)^2$

Correlation of activity coefficient and density data

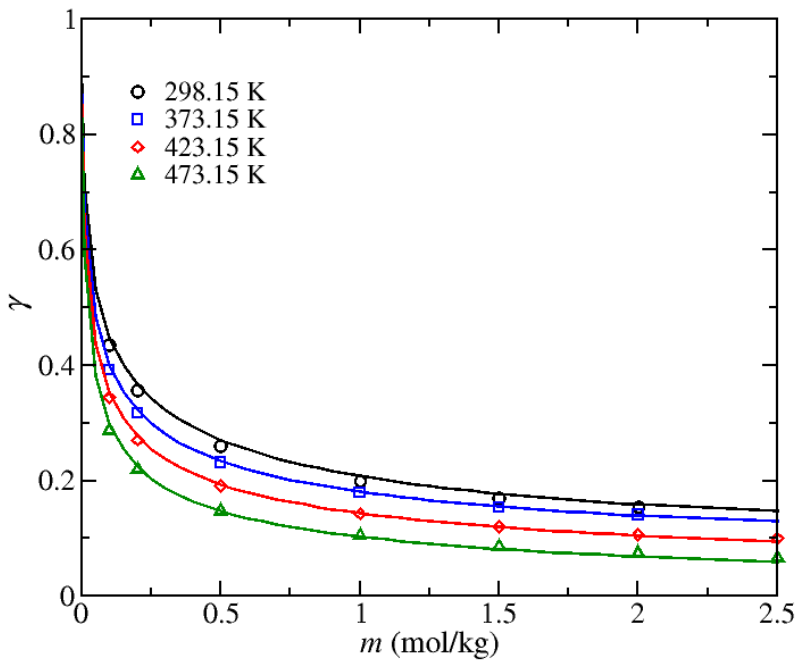
Salt	Max. molality (mol/kg)	AAD% (γ)	AAD% (ρ)
NaCl	6.0	1.87	0.61
KCl	5.0	1.93	0.23
$CaCl_2$	5.0	1.89	0.46
$MgCl_2$	3.0	2.31	1.49
Na_2SO_4	3.0	2.03	1.20
K_2SO_4	2.5	2.04	1.14
NaBr	5.0	2.02	1.67
KBr	5.0	2.46	1.90

Activity coefficient of single salt solutions

Aqueous NaCl solution



Aqueous K_2SO_4 solution

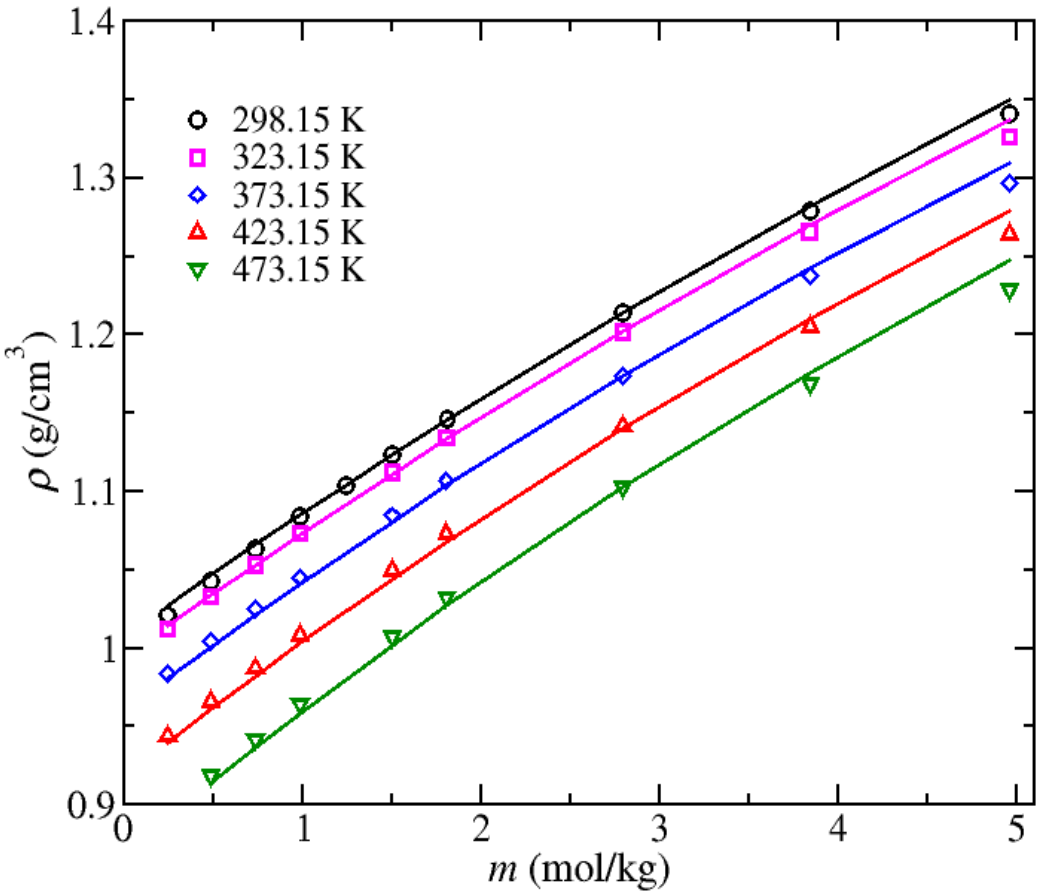


Points: Expt data

Lines: SAFT2-KMSA correlations

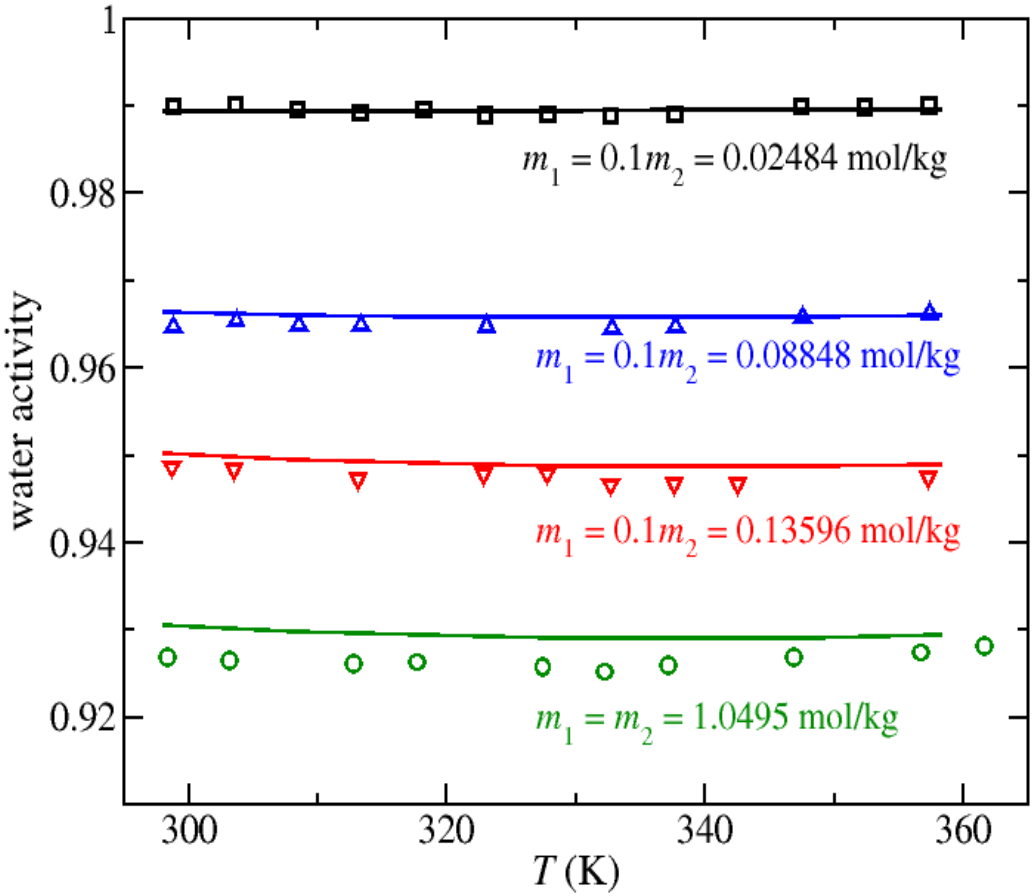
Density of electrolyte solutions

Aqueous $CaCl_2$ solution



Activity in mixed salt solutions

Activity of H_2O in mixed NaCl (1) – Na_2SO_4 (2)



Binary interaction parameters

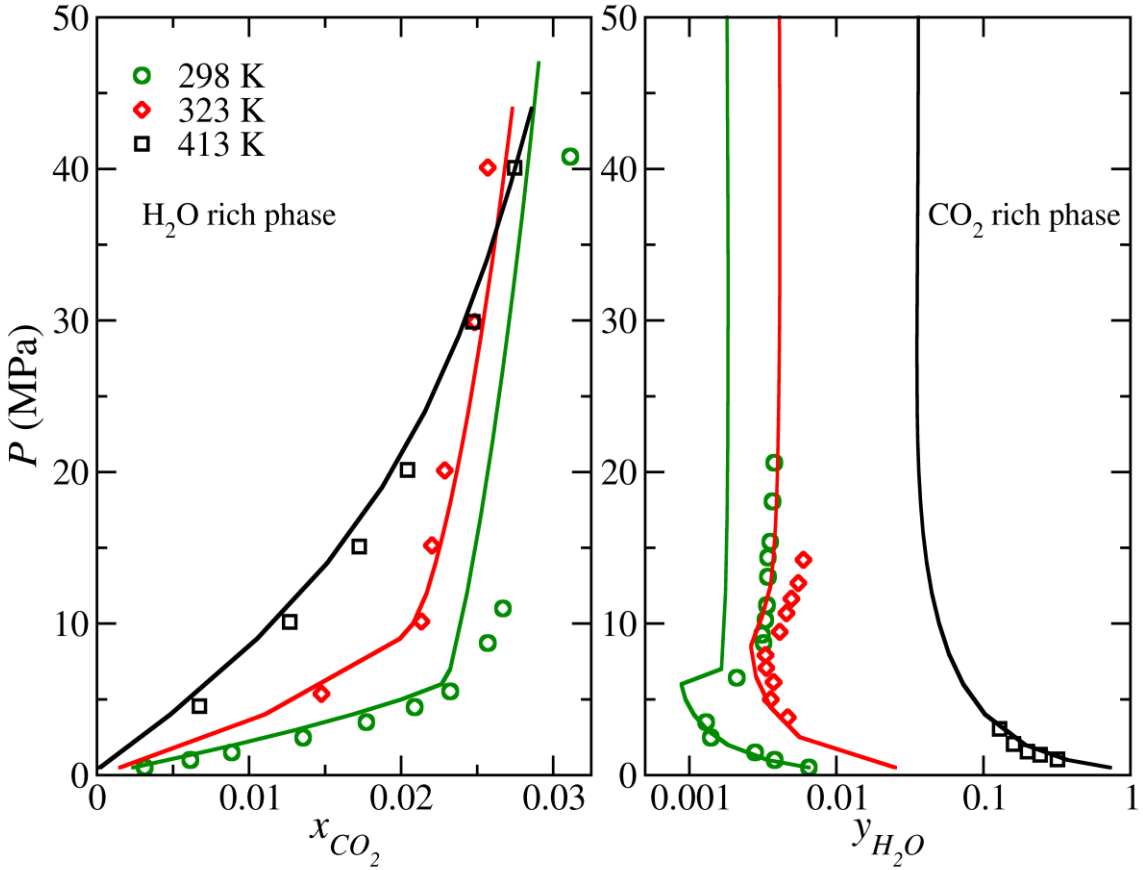
- For $CO_2 - H_2O$ and CO_2 – ion temperature dependent k_{ij} are used: $k_{ij} = c_0 + c_1 T$

	c_0 (-)	c_1 (K^{-1})
$CO_2 - H_2O$	0.0977	2.6110^{-4}
$CO_2 - Na^+$	0.2047	-4.7910^{-5}
$CO_2 - K^+$	-0.3970	-1.8110^{-5}
$CO_2 - Ca^{2+}$	-0.0011	1.2110^{-4}
$CO_2 - Mg^{2+}$	-0.0183	1.2610^{-3}
$CO_2 - Cl^-$	-0.0249	9.3110^{-6}
$CO_2 - SO_4^{2-}$	0.2072	7.1710^{-4}

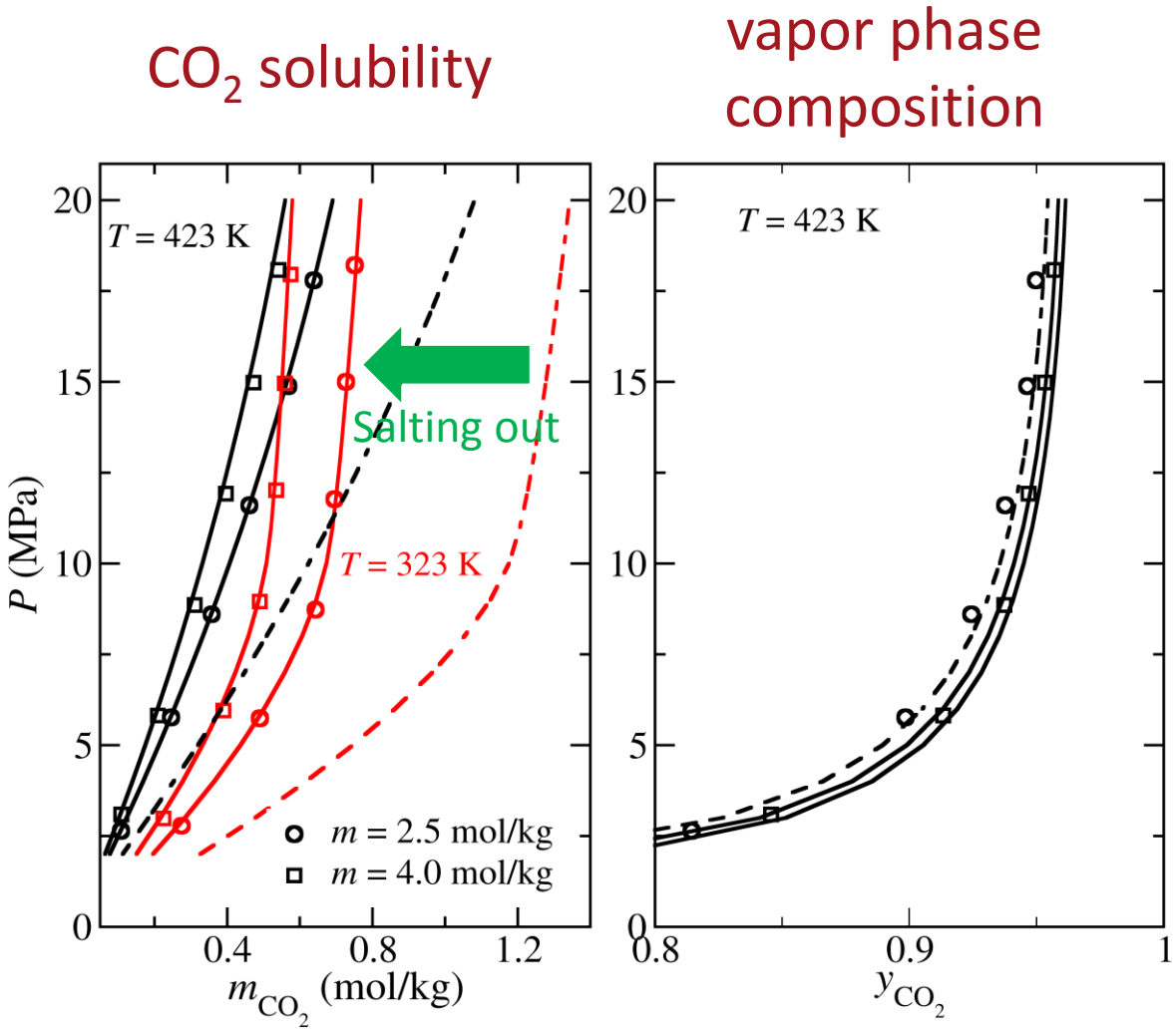
CO_2 – H_2O phase equilibria

CO_2 solubility in H_2O

H_2O solubility in CO_2

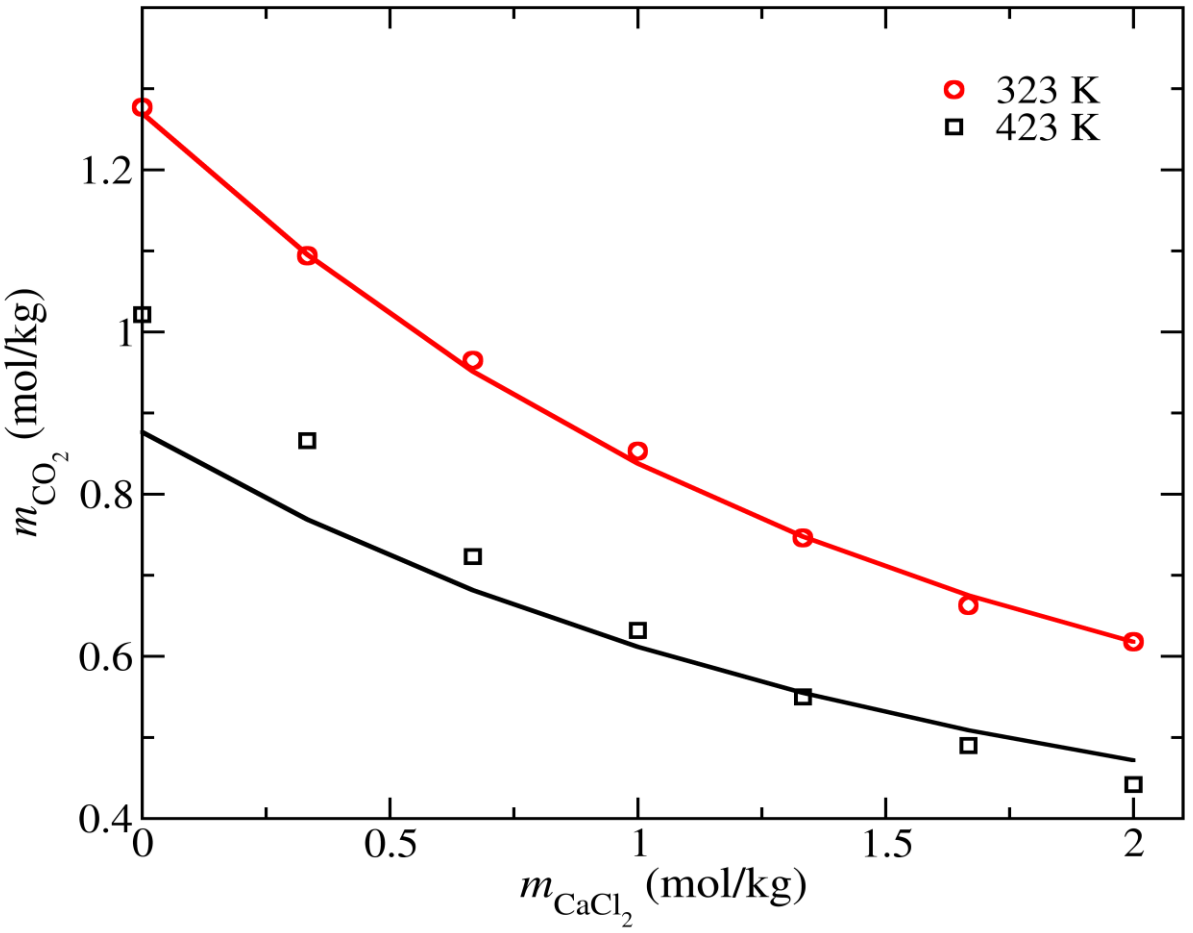


CO_2 solubility in aqueous NaCl solutions



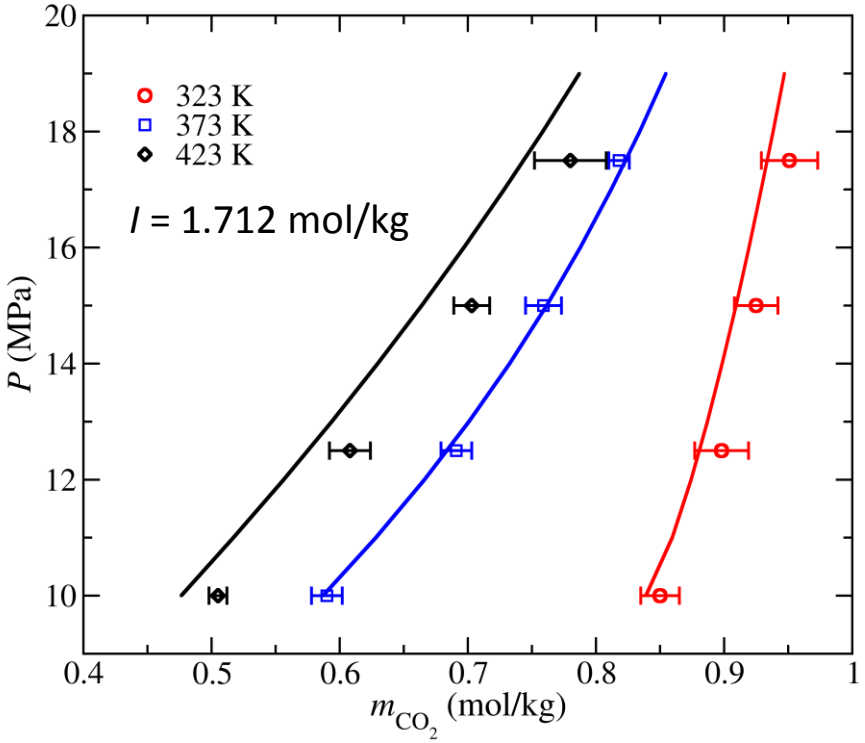
Dashed lines: Salt-free model predictions

CO_2 solubility in aqueous $CaCl_2$ solutions

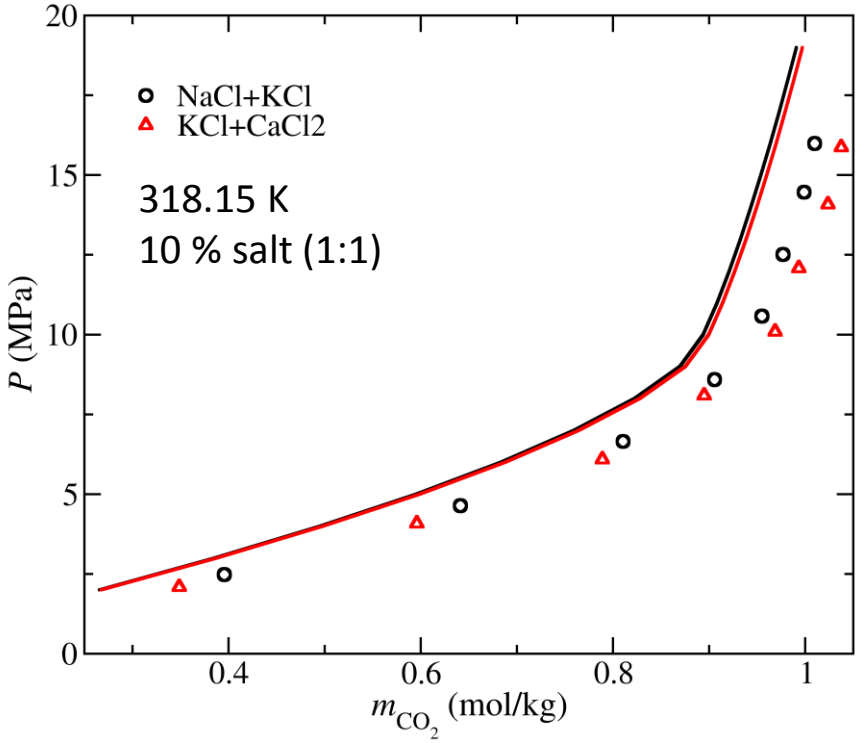


CO_2 solubility in mixed salt solutions

CO_2 solubility in mixed NaCl + $CaCl_2$

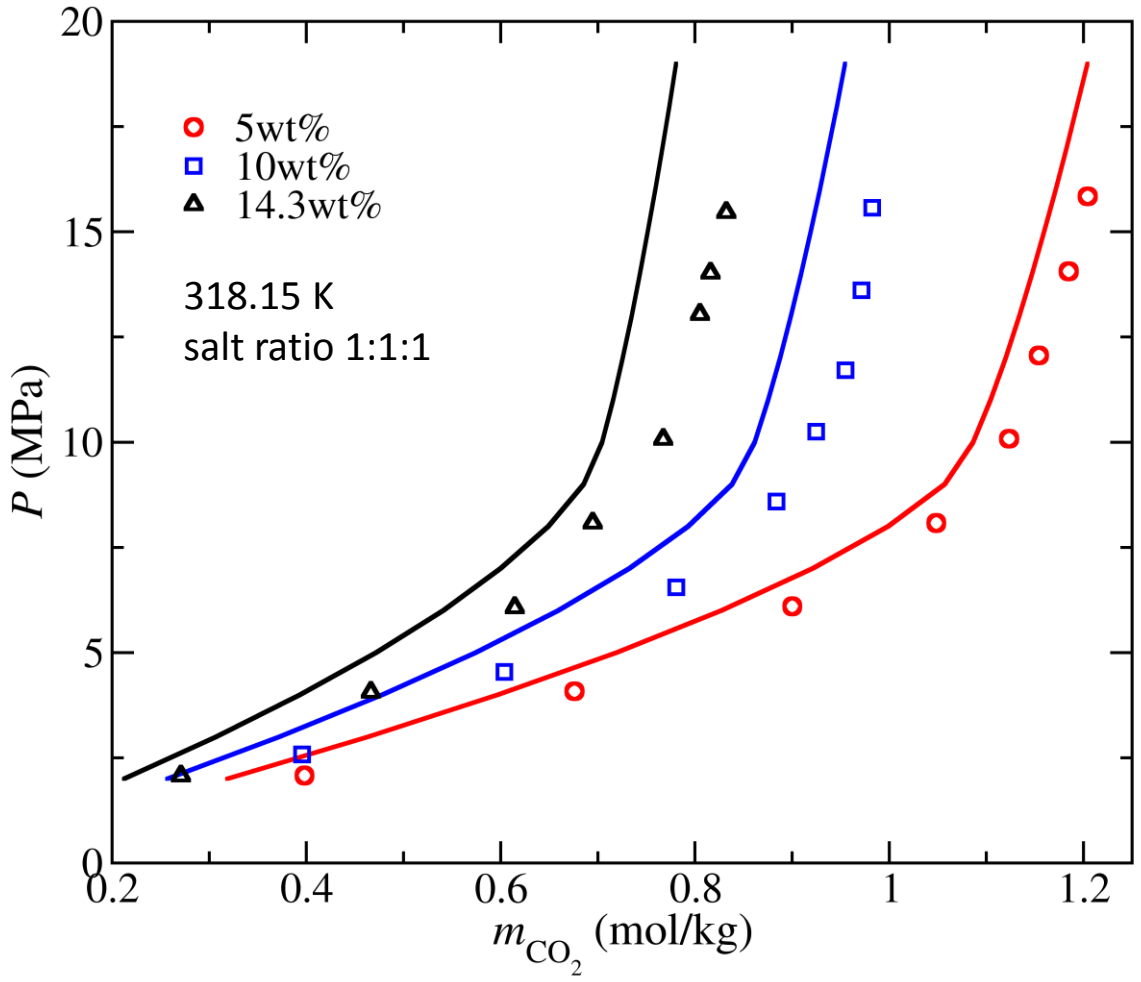


CO_2 solubility in mixed NaCl + KCl (or $CaCl_2$)

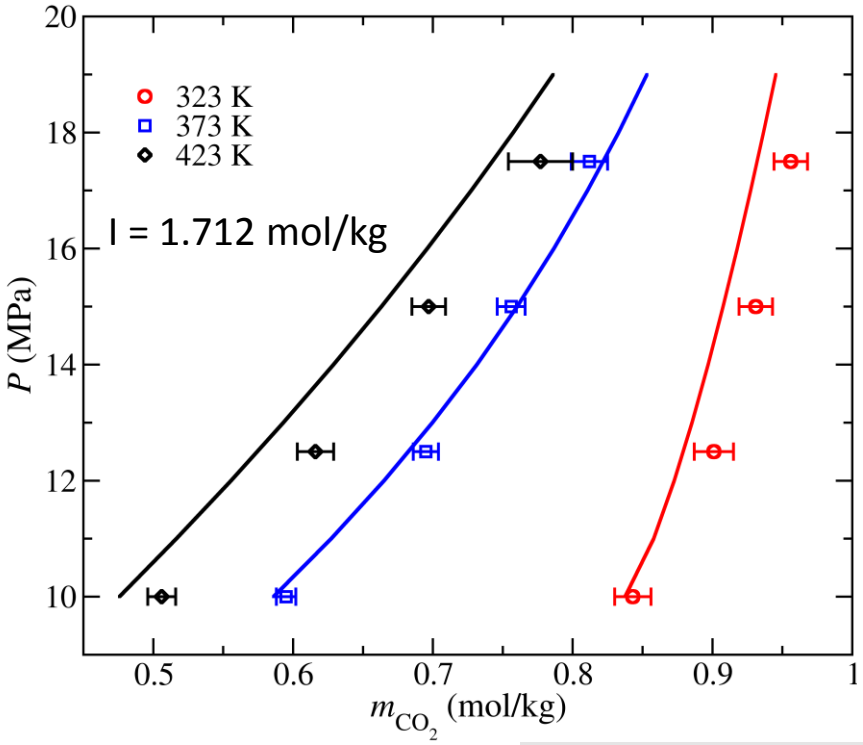


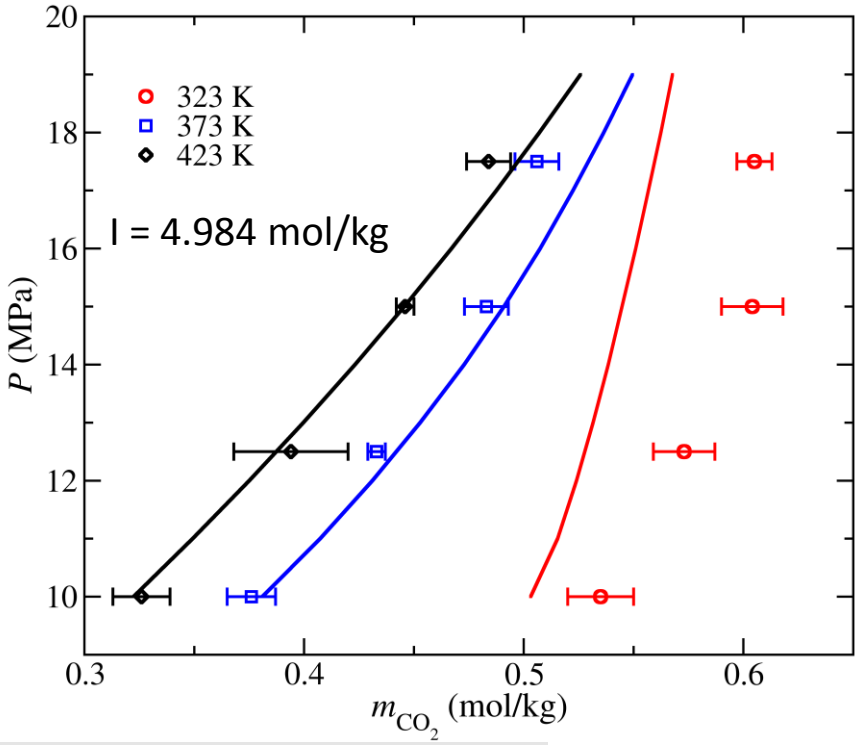
$$I = \sum_i m_i z_i^2$$

CO_2 solubility in mixed NaCl + KCl + $CaCl_2$ solutions



CO_2 solubility in synthetic brines





Zhao *et al.*, *Environ. Sci. Techol.* 49, 1972 (2015)

	synthetic Mt. Simon formation brine (mol/kg H_2O)		synthetic Antrim Shale formation brine (mol/kg H_2O)	
salt species	proxy brine 1[a]	proxy brine 2[b]	proxy brine 1[a]	proxy brine 2[b]
NaCl	1.0601	1.0601	2.9856	2.9856
$CaCl_2$	0.1365	0.2172	0.3937	0.6661
Na_2SO_4	0.0165		0.0001	
$MgCl_2$	0.0544		0.2535	
KCl	0.0188		0.0222	
$SrCl_2$	0.0021		0.0083	
NaBr	0.0042		0.0090	
I	1.712		4.984	

Conclusions

- An improved mean spherical approximation formalism was incorporated in SAFT EoS.
- The new SAFT2-KMSA correlates accurately the activity coefficient and liquid densities of electrolyte solutions at various temperatures.
- CO_2 solubilities in H_2O and single electrolyte solutions were accurately correlated.
  - T-dependent k_{ij} for $CO_2 - H_2O$ and CO_2 – ion interactions.
- The model predicts accurately the CO_2 solubility in mixed electrolyte solutions and brines without any additional parameter.
- The new model can be used reliably for CCS process design.

Acknowledgments

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Reference: H. Jiang, A.Z. Panagiotopoulos and I.G. Economou, *Geochimica et Cosmochimica Acta,* in press (2016).