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The Application of the "Mean Spherical Approximation" Approach for Natural Gas-Brine Mixtures

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Scopes

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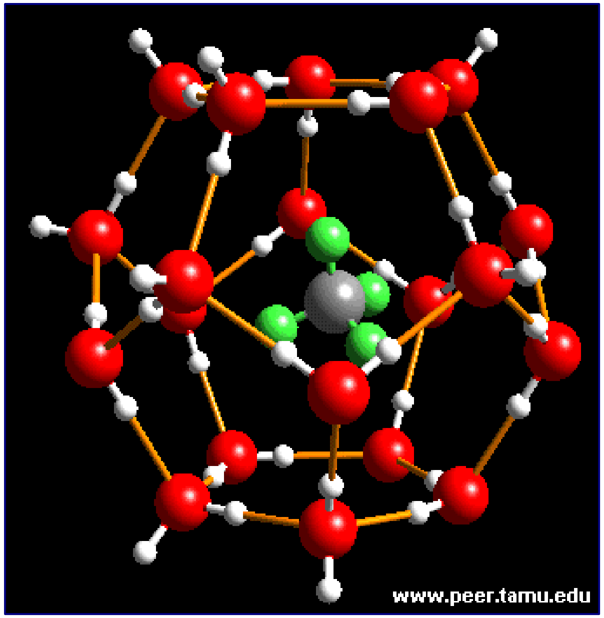
What is the "Gas Hydrate"?

"Gas Hydrates" are crystalline water based solids containing light gases (O_2, H_2, N_2, CO_2, H_2S...) and hydrocarbons (CH_4, C_2H_6...) trapped inside "cages" of hydrogen bonded water.



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The Objectives

To propose a simple, practical, and accurate model for prediction of hydrate equilibrium conditions in electrolyte solutions.

Challenges:

- The temperature effect
- Amount and the effect of dissolved gas
- Its value in mixed electrolytes

The Base Model

$$\mu_W^H = \mu_W^L$$

$$\frac{\Delta\mu_W^0}{RT_0} - \int_{T_0}^{T} \left(\frac{\Delta h_W}{RT^2}\right) dT + \left(\frac{\Delta v_W}{RT}\right) P - \sum_i v_i \ln\left(1 + \sum_j C_{ij} f_j\right) - \ln(a_W) = 0$$

T, P: Hydrate formation Temperature, Pressure

a_w: Water activity in the liquid phase

F_j: Fugacity of hydrate dormer j in gas phase

C_{ij}: Langmuir constant

T_0: Reference temperature, 273.15 K.

R: Universal gas constant

$\triangle$: Difference with hypothetical empty hydrate phase

h_w: Enthalpy for the water phase

v_w: Water specific volume

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Electrolyte Models

➢ **The Mean Spherical Approximation (GV-MSA) Model**

Advantages: Accurate, adjustable parameters with physical interpretation, capable to be extended for more complex mixtures.

Disadvantage: complex, iterative, need for the mixture density.

$$\ln \gamma_i = \left(\frac{\mu_i^r}{kT}\right)^{hs} + \left(\frac{\mu_i^r}{kT}\right)^{elec}$$

$$\left(\frac{\mu_i^r}{kT}\right)^{elec} = \frac{z_i e^2}{\varepsilon kT}\left(\frac{2\Gamma a_i}{\sigma_i \alpha^2} - \frac{z_i}{\sigma_i}\right)$$

$$\left(\frac{\mu_i^r}{kT}\right)^{hs} = \left[\begin{array}{l} \frac{A^r}{NkT} + \frac{3M_{1,i}}{4}K_1 + \frac{3}{2}\left(\frac{2M_{2,i} - M_{1,i}}{4}\right)K_2 + \\ \left(\frac{1+3Y_1}{4}\right)\left(\frac{\partial K_1}{\partial \rho_i}\right)_{T,V,\rho_{j \neq i}} + \frac{3}{2}\left(\frac{2Y_2 - Y_1 - 1}{4}\right)\left(\frac{\partial K_2}{\partial \rho_i}\right)_{T,V,\rho_{j \neq i}} \end{array}\right]$$

Adjustable Parameters

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The Temperature Effect

- First we calculate the adjustable parameters at a reference temperature (25 °C or 0 °C) by minimizing the average absolute deviation between the results of the model and the experimental data. Then we extend the model with respect to the temperature deviation as:

$$AP_T = AP_{T_0}(1+\eta_1\theta+\eta_2\theta^2)$$

- AP_T: Adjustable Parameter at T
- AP_{T0}: Adjusted value of *AP* at the reference temperature.
- θ: Temperature deviation parameter, for instance T^2-T_0^2.
- η: New Adjustable Parameters which should be calculated.

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The Temperature Effect

$$\sigma_{25}^{+} = \sigma_{25,0} + \lambda_{25,1} c$$

$$\varepsilon = \frac{\varepsilon_0}{(1 + \lambda_{25,2} c)}$$

$$\sigma_{T,0} = \sigma_{25,0}(1 + \eta_1 \theta)$$

$$\lambda_{T,1} = \lambda_{25,1}(1 + \eta_2 \theta + \eta_3 \theta^2)$$

$$\lambda_{T,2} = \lambda_{25,2}(1 + \eta_4 \sqrt{|\theta|})$$

$$\theta = (\frac{298.15^2 - T^2}{T})$$

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The Effect of Dissolved CO_2

From the GV-MSA Model

From the Peng-Robinson EOS

$$\mu_{CO2}^{L} = \mu_{CO2}^{V}$$

- By:

1. Including CO_2 molecule as neutral hard sphere (i.e. zero electrostatic contribution) in NaCl solution and calculating the hydrated diameter of CO2 as a function of temperature and concentration by using CO2 solubility data.

2. Extending the model for mixed electrolytes by assuming that the proportional CO2 solubility inhibition effects of different salts with respect to NaCl might keep almost constant at different temperatures and pressures.

Water Activity in Single Electrolytes

$$\ln a_W = (-v_s.m.M_S.\phi)/1000$$

$$\phi = 1 + \frac{1}{m}\int_0^m m(\frac{\partial \ln \gamma_m}{\partial m})dm$$

v_s: Number of produced ions in water

m: Molality (mol salt/1 kg water)

M_s: Water molecular weight

Φ: Osmotic Coefficient

γ_m: Mean inonic activity coeffcient (from Pitzer model).

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Water Activity in Mixed Electrolytes

$$\ln a_{W,mix} = (-v_{s,mix}.m_T.M_S.\phi_{mix})/1000$$

$$m_T = \sum_{i=1}^{N} m_i \qquad v_{s,mix} = \sum_{i=1}^{N} (\frac{m_i}{m_T}) v_{s,i}$$

$$\phi_{mix} = \sum_{i=1}^{N} (\frac{I_i}{I_T}) \phi_i^* \qquad m_i^* = \sum_{i=1}^{N} (\frac{m_i}{I_i}) I_T$$

$v_{s,mix}$: Number of ions produced

m_T : Total Molality

Φ: Mixture Osmotic Coefficient

M_s: Water molecular weight

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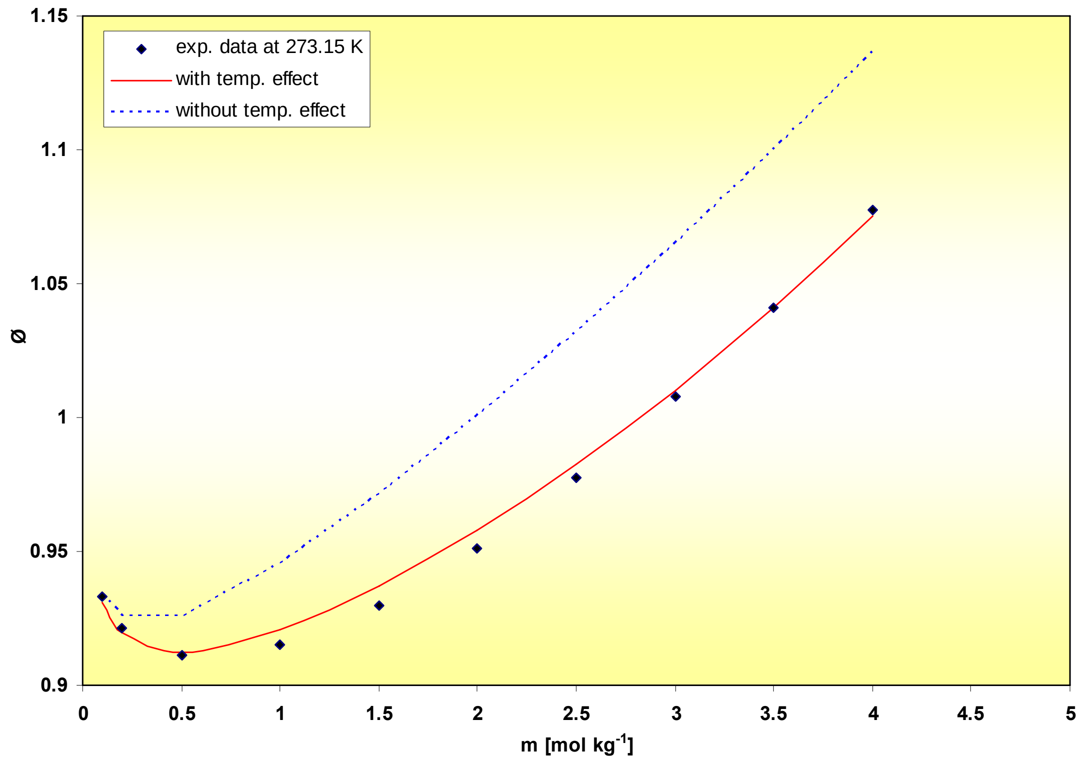
Results

Electrolyte	GV-MSA App-1	GV-MSA App-2	GV-MSA App-3	Pitzer	m_{max} (mol kg^{-1})
Nacl	0.14	0.13	0.38	0.12	6
Kcl	0.08	0.04	0.3	0.07	5
NaBr	0.16	0.14	0.34	0.18	5
LiCl	0.08	0.11	0.31	0.05	5
CsCl	0.04	0.07	0.04	0.04	6
KBr	0.15	0.11	0.33	0.13	5
$NaClO_3$	0.02	0.04	0.09	0.05	2
$NaClO_4$	0.03	0.02	0.1	0.07	2
NH4Cl	0.04	0.06	0.14	0.05	5
$NH4NO_3$	0.05	0.1	0.05	0.05	5
$CaCl_2$	0.89	0.51	1.11	1.57	6
$BaCl_2$	0.18	0.2	0.22	0.13	1.5
$ZnCl_2$	0.22	0.51	0.08	0.22	1
$SrCl_2$	0.28	0.38	0.21	0.08	2
$MgSO_4$	1.84	1.96	1.54	3.14	3.5
NaF	0.03	0.02	0.07	0.03	1
NaI	0.05	0.11	0.36	0.07	10
LiBr	0.07	0.07	0.18	0.15	5
$LiNO_3$	0.22	0.2	0.56	0.62	5
KI	0.05	0.08	0.02	0.02	2
CsBr	0.03	0.04	0.07	0.04	5
$MgCl_2$	0.3	0.51	0.81	0.45	5
$K2SO_4$	0.05	0.08	0.1	0.01	0.7
$Na2SO_4$	0.44	0.65	1.32	0.81	4.5
Average	0.23	0.26	0.36	0.34	

Electrolyte	Parameters of the App-1 at 25 °C: $\sigma_{25,0}$ (Å)	$\lambda_{25,1}$ (Åmol^{-1}L)	$\lambda_{25,2}$ (mol^{-1}L)	m_{max} (mol kg^{-1})	AARD %
Nacl	3.9161	-0.0331	0.1223	6	0.14
Kcl	3.5654	-0.0089	0.1334	5	0.08
NaBr	3.9675	-0.0476	0.1104	5	0.16
LiCl	4.9949	-0.0901	0.1676	5	0.08
CsCl	2.0182	0.0700	0.0133	6	0.04
KBr	3.3499	-0.0291	0.1020	5	0.15
$NaClO_3$	4.3507	0.0201	0.2492	2	0.02
$NaClO_4$	4.4329	-0.0166	0.2147	2	0.03
NH4Cl	3.6194	-0.0176	0.1306	5	0.04
$NH4NO_3$	3.0514	-0.0016	0.0493	5	0.05
$CaCl_2$	6.3491	-0.1501	0.1256	6	0.89
$BaCl_2$	5.0914	-0.1530	0.0053	1.5	0.18
$ZnCl_2$	6.1161	-1.0106	0.1964	1	0.22
$SrCl_2$	5.4723	-0.1485	0.0471	2	0.28
$MgSO_4$	4.7824	0.1271	0.0208	3.5	1.84
NaF	4.0668	0.1317	0.2391	1	0.03
NaI	4.2356	-0.0701	0.1573	10	0.05
LiBr	4.8839	-0.0692	0.1251	5	0.07
$LiNO_3$	7.3102	-0.3312	0.4213	5	0.22
KI	3.4923	-0.0929	0.1227	2	0.05
CsBr	2.0189	0.1161	0.0596	5	0.03
$MgCl_2$	6.4175	-0.2325	0.1067	5	0.3
$K2SO_4$	2.8462	-1.3638	-0.1248	0.7	0.05
$Na2SO_4$	4.5394	-0.0116	0.2435	4.5	0.44
Average					0.23

Results

Temperature effect and the modified GV-MSA model:



The osmotic coefficient of NaCl solution at 273.15 K, using the modified and original MSA model.

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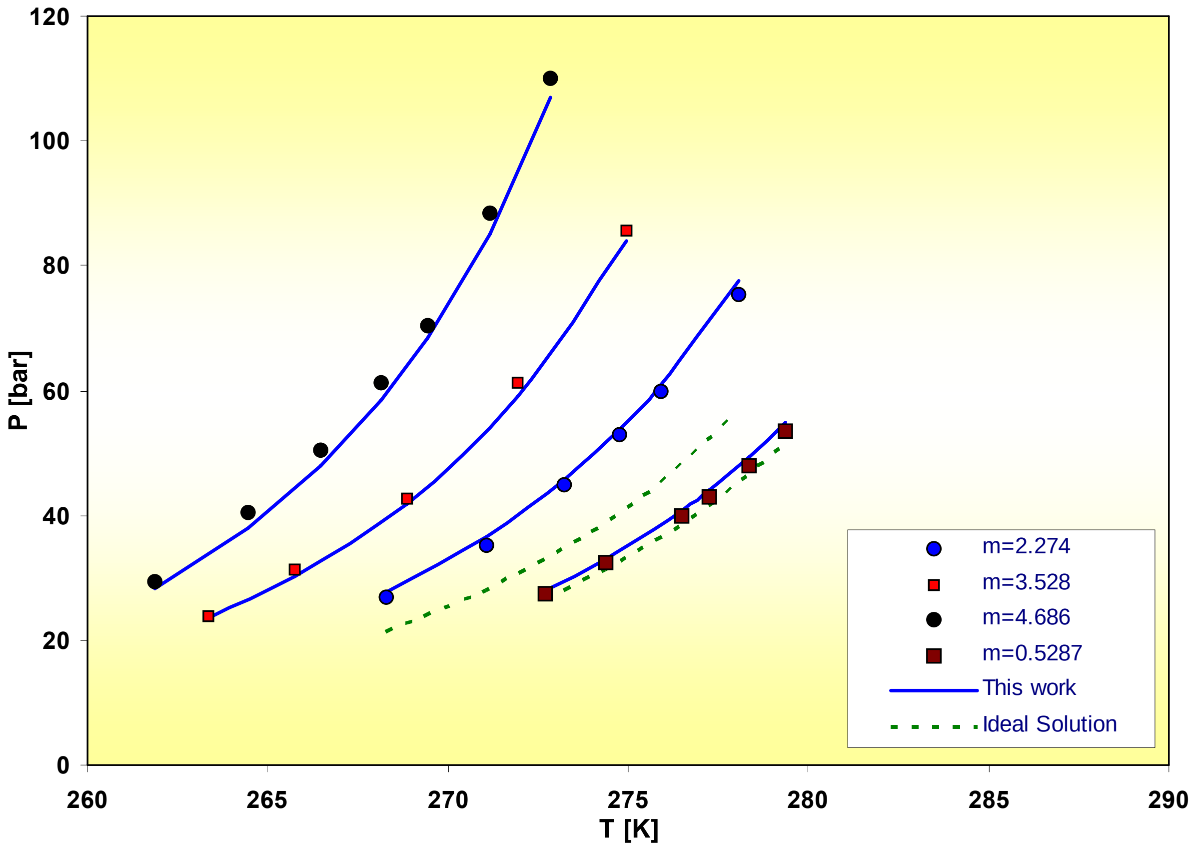
Methane Hydrate in NaCl Solution



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Conclusions

- **MSA based models are capable approaches to be applied for complex mixtures.**

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Thank You