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Crossover soft-SAFT modelling of vapour-liquid equilibrium of CO₂ – NO₂/N₂O₄ mixture

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OBJECTIVE

Accurate thermo-physical properties are mandatory for all industrial applications. However, experimental data are often scarce and models are needed for the estimation of properties. Such is the case in supercritical processes like the selective oxidation of vegetal macromolecules in mixture NO₂/N₂O₄ – supercritical CO₂ aiming at producing body-degradable polymers readily usable for inside body surgery. The so-called crossover soft-SAFT equation of state is used to calculate the liquid vapor equilibrium curves especially in order to evaluate near and above the critical region the amount of NO₂ monomer that is the oxidizing agent.

The crossover soft-SAFT Equation of State model

1. General expression of SAFT EoS

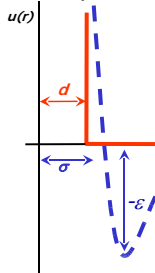
$$a^{SAFT} = a^{real} - a^{ideal}$$

$$= a^{ref}(m, \rho, T; \sigma, \epsilon) + a^{chain}(\rho, T, X_i; \sigma_i, \epsilon_i, m_i)$$

$$+ a^{assoc}(\rho, T, X_i; \sigma_i, \epsilon_i, \epsilon^{\alpha\beta}, K^{\alpha\beta})$$

$$+ \dots + a^{polar}(\rho, T, Q, \mu)$$

Reference potential



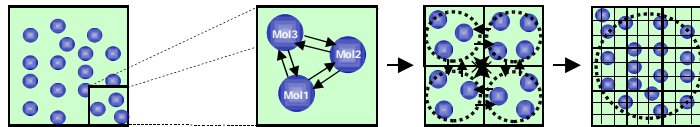
Statistical Associating Fluid Theory (SAFT) : SAFT is a very successful theory to describe the phase behavior of complex fluids and it has shown to quantitatively predict several complex mixtures. The soft-SAFT equation is one of the variants of the original SAFT that uses a Lennard-Jones model to describe the interaction between molecules.

SAFT Original by Chapman et al. 1989:
hard sphere

soft-SAFT by Vega L. et al. 2000:
Lennard Jones

2. Handling the critical point region requires accounting for density fluctuations (Wilson et al. 1971)

2.1. The phase-space cell approximation is a technique employed to consider the long-range property fluctuations



- Modelling of a fluid with several molecules, A small cell of length L is selected.
- The properties of the small cell is calculated by applying mean field theory.
- Each cell interacts with its neighbors using again a mean field theory.
- The procedure is repeated till the whole amount of molecules is considered.

2.2. Crossover for phase equilibria properties

$$a^{crossover} = a^{soft-SAFT} + \sum_{j=1}^5 \frac{f^{crossover}}{\rho}$$

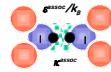
$$f^{crossover} = -K_n \ln \left(\frac{\Omega_{2n}^c}{\Omega_{2n}^n} \right)$$

- Crossover parameters:
- L: Cut off Length
 - Φ: Crossover parameter

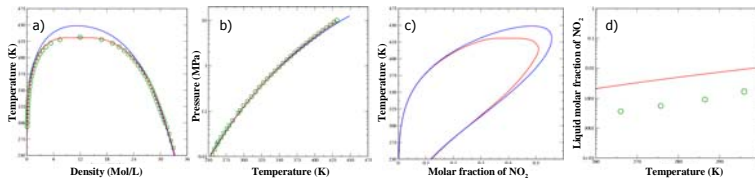
A set of recursive relations are written where the contributions of wavelength fluctuations are successively taken into account in the free energy density. In this way, properties approach the asymptotic behavior in the critical region and they exhibit a crossover between the classical and the universal scaling behavior in the near critical region by the use of the crossover treatment.

Reacting system : 2 NO₂ ⇌ N₂O₄

- Interest in biological and environmental Chemistry
- single associating site localized on N (association type 1A) strong self association



VLE region of the reacting system NO₂-N₂O₄



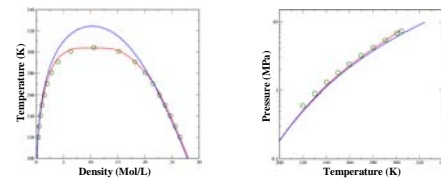
experimental data: a) and b) (●) Reamer & Sage, 1952 (□) Glaue & Kemp, 1938 c) and d) (○) James and Marshall, 1968

Polar molecule : CO₂

- Supercritical CO₂ used as solvent in extraction process.
- The quadrupole moment Q(μ) is included and improves the prediction of the behavior of CO₂ in mixtures.



VLE region of pure CO₂



experimental data: (○) NIST, 2006

The mixture CO₂ + NO₂/N₂O₄

The prediction of CO₂ + NO₂ / N₂O₄ mixtures vapor – liquid equilibrium properties is of utmost importance to assess correctly the NO₂ monomer amount that is the oxidizing agent of vegetal macromolecules in the CO₂ – NO₂ / N₂O₄ reacting medium, leading to the production of body-degradable polymers readily usable for inside body surgery.

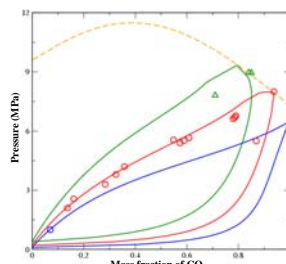
Molecular parameters

	m	σ (Å)	ε/k _B (K)	Φ	L/σ	Q (C.m ²)	ε ^{off} /k _B (K)	ε ^{off} (Å ³)
CO ₂	1.606	3.174	158.5	5.70	1.130	4.4.10 ⁻⁴⁰	NA	NA
NO ₂	1.295	3.200	247.8	6.50	1.172	NA	6681	1.0

Combining rules

$$\sigma_{ij} = \eta_{ij} \frac{\sigma_i + \sigma_j}{2} \quad \text{For CO}_2 + \text{NO}_2/\text{N}_2\text{O}_4 \quad \eta = 1.00$$

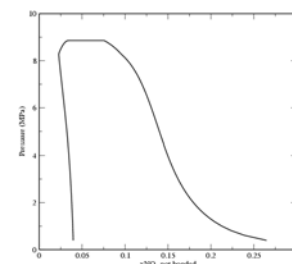
$$\epsilon_{ij} = \xi_{ij} \sqrt{\epsilon_i \epsilon_j} \quad \xi = 1.05$$



Crossover soft-SAFT predictions

experimental data

- 298.15 K (●) Camy et al. 2006
- 313.15 K (○) Camy et al. 2006
- 328.45 K (○) Camy et al. 2006
- critical line calculated by crossover soft-SAFT



Molar fraction of NO₂ not bonded in the vapour-liquid equilibrium of the mixture CO₂+NO₂/N₂O₄ at 313.15K

Conclusion

The crossover soft-SAFT version EoS has permitted a prediction of the physicochemical properties of the reacting system NO₂-N₂O₄ + CO₂ at subcritical and supercritical conditions. The need of a unique binary parameter to describe this complicated mixture at several temperatures shows the capability of the equation to model complex mixtures near to and far from the critical region.