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An Equation of State for Solid-Liquid-Vapor Equilibrium Applied to Gas Processing and Liquefied Natural Gas

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Introduction

Cryogenic processes are widely used in natural gas industry for the production of liquefied natural gas.

Many efforts are made by the Liquefied Natural Gas (LNG) producing companies to ensure the safety of their plants. Despite the use of purification units, traces of pollutants can remain. These unwanted substances can form a mass of solid deposit causing dysfunctioning of the gas processing units.

In order to avoid these problems in the industrial cryogenic processes involving natural gas treatment, the accurate knowledge of thermodynamic properties like solid-liquid, liquid-vapor and solid-vapor equilibria is of a great importance.

We present a thermodynamic model, the Solid-Liquid-Vapor Peng-Robinson Equation of State (SLV PR EoS), suitable for being applied in the simulation of gas processing and LNG production thanks to its capability of accounting for the solid phase and the solid-fluid equilibrium.

This model has been used for representing phase equilibria of some pure compounds and binary mixtures of interest in the gas processing and LNG production.

Thermodynamic model

Yokozeki [1] proposed the first EoS introducing a discontinuity in the solid-fluid transition region. This EoS presents a fourth power of volume, which allows representing all the three phases of matter with a single functional form. The fourth root is the common unphysical volume placed under the S-loop connecting the liquid and the vapor regions.

The SLV PR EoS has been obtained starting from the Yokozeki EoS in which the Peng-Robinson's attractive term has been considered; this EoS is defined as follow:

$$P(T, v) = \frac{RT}{v - c(T)} \left(\frac{v - d}{v - b} \right) - \frac{a(T)}{v^2 + 2bv - b^2}$$

P : pressure T : temperature R : gas constant v : volume
 a, d : parameters b : liquid covolume c : solid covolume

The proposed EoS has been used for representing phase equilibria of some pure compounds (Kr, CO₂, CH₄, C₂H₆, and C₃H₈) and binary mixtures usually involved in gas processing and LNG production.

Results for Pure Components

A pressure-temperature range has been fixed for each pure compound; each range extends from a minimum to a maximum, located on the SVE and the SLE branches, respectively. These values are indicated in Table 1. The VLE branch is instead studied between the triple and the critical points for all the pure compounds. For ethane and propane the lower limits correspond to the triple point coordinates.

Fluid	SVE		SLE	
	Tmin / K	Pmin / Pa	Tmax / K	Pmax / MPa
Kr	66	12	220	430
CO ₂	170	10 ⁶	310	640
CH ₄	60	16	200	600
C ₂ H ₆	90.359	1.14	340	4100
C ₃ H ₈	85.53	1.7×10 ⁴	380	4160

Table 1: P-T ranges for the pure compounds studied.

The quantitative comparison of the phase equilibrium values obtained with the SLV PR EoS and those from auxiliary equations [2] has been evaluated with reference to the common statistical indexes: AAD%, Bias% and MAD%. Table 2 represents these errors obtained calculating the equilibrium temperature at fixed pressure, for the compounds reported in Table 1.

Fluid	VLE			SVE			SLE		
	AAD %	BIAS %	MAD %	AAD %	BIAS %	MAD %	AAD %	BIAS %	MAD %
Kr	0.07	-0.02	0.16	0.61	-0.61	2.02	0.19	-0.04	0.69
CO ₂	0.04	-0.01	0.09	1.19	-1.19	4.29	0.24	-0.09	0.62
CH ₄	0.07	-0.02	0.16	0.36	0.36	0.49	0.13	-0.03	0.32
C ₂ H ₆	0.08	-0.01	0.22				0.03	0.01	0.07
C ₃ H ₈	0.11	-0.02	0.24				1.41	-0.30	3.65

Table 2: Summary of the statistical errors in calculating SVE, SLE, and VLE with the SLV PR EoS.

Results for Methane + Krypton Binary System

In this work, we present the qualitative comparison between the SLV PR EoS and experimental values concerning the CH₄ + Kr mixture.

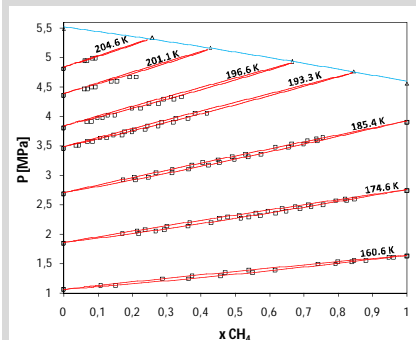


Figure 1: Isothermal P-x VLE behaviors. 161 K ≤ T ≤ 205 K. Calculated values: — VLE; — critical line. Data (□): VLE (△); critical line (△).

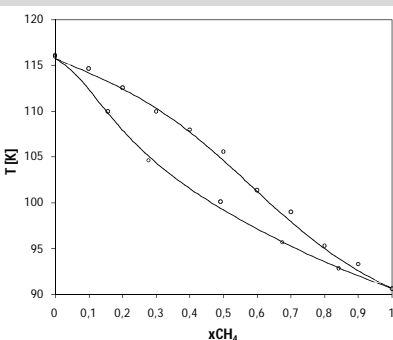


Figure 2: Isobaric T-x SLE behavior. Calculated values: — SLE. Data: □: Veith and Schröder [4].

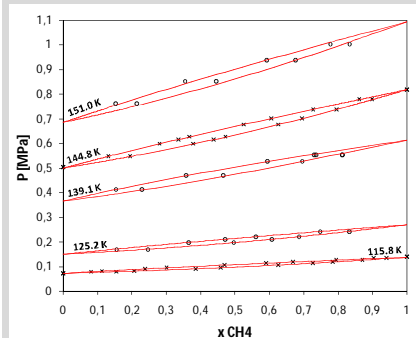


Figure 3: Isothermal P-x VLE behaviors. 116 K ≤ T ≤ 151 K. Calculated values: — VLE. Data: □: Holcomb and Zollweg [5]; ×: Calado and Staveley [6].

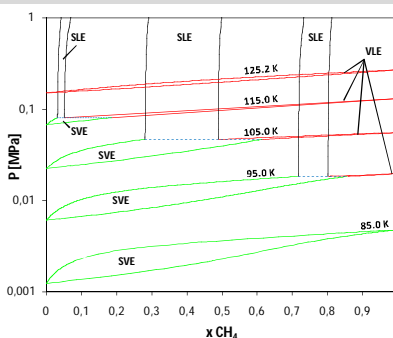


Figure 4: Isothermal P-x VLE, SVE, and SLE behaviors. Calculated values: — SLE; — VLE; — SVE; — triple pressure.

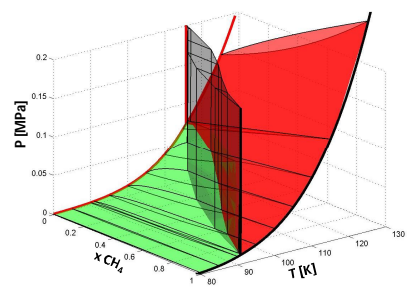
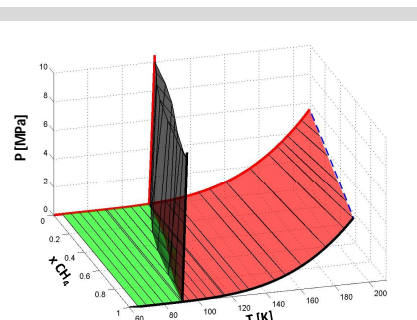


Figure 5: P-T-x equilibrium behaviors. Calculated values: — CH₄; — Kr. Isothermal P-x cross sections: ■ VLE; ■ SLE; ■ SVE.

Conclusion and Perspectives

The SLV PR EoS allows a good representation of the SLE, SVE, and VLE in a wide range of temperature and pressure for different compounds of interest in the gas processing and LNG production. The intention of the authors is to extend the study to other pure compounds and to reduce the number of the parameters included in the SLV PR EoS for an industrial application of this equation. The EoS proposed can be extended to mixtures, and allows evaluating their thermodynamic behavior in the cryogenic field.

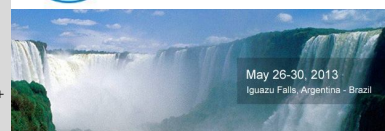
This should be an important aid for designing and optimizing industrial cryogenic processes; knowing at which conditions in a mixture the solid-fluid equilibria appears (where fluid means either the liquid or the vapor phase) represents an opportunity of great interest, because it could be used for improving the process design and for avoiding some drawbacks as solidification of the impurities. The phase diagrams, as Px and Tx cross sections at cryogenic conditions, can give important information for evaluating new separation techniques, exploiting the capability of the SLV PR EoS in representing phase equilibrium values in which also the solid phase is involved.

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