

**CONSTRAINING THE SOURCES OF UNCERTAINTY OF THE RST THERMODYNAMIC MODEL APPLIED TO TITAN.** T. Cornet<sup>1</sup>, D. Cordier<sup>2</sup>, N. Marounina<sup>3</sup>, T. Le Bahers<sup>4</sup>, and N. Altobelli<sup>1</sup>, <sup>1</sup>European Space Agency (ESA/ESAC), Madrid, Spain ([tcornet@sciops.esa.int](mailto:tcornet@sciops.esa.int)). <sup>2</sup>Laboratoire GSMA, Université de Reims, Reims, France. <sup>3</sup>LPG Nantes, UMR 6112 CNRS, Université de Nantes, Nantes, France. <sup>4</sup>ENS, Université de Lyon 1, Lyon, France.

**Introduction:** Saturn's moon Titan possesses a diverse geology including liquid hydrocarbon rivers, lakes and seas, which results from the erosion of the solid surface by rains. Among the erosional processes, dissolution could play a major role on Titan [1]. This motivates strong effort to develop thermodynamic models as accurate as possible in order to describe these surface-atmosphere interactions. The most recently used models are the Regular Solution Theory (RST) [1,2], the modified Van Laar (mVL) [3] and the (polar-)PC-SAFT [4,5,6].

All of these models suffer from the same limitation: the need to adjust free binary interaction parameter(s) to experimental data of solid-liquid or liquid-vapor binary systems. Many systems on Titan would involve mixtures of complex organics in liquid hydrocarbons, for which no laboratory experiments have been reported so far. In the present work, we try to provide constraints on two sources of uncertainty of the RST model calculations in the frame of the solid-liquid equilibrium (SLE): the molar volumes of the pure components forming a mixture (involved in solubility parameter and dissolution rate calculations [1]), and the binary interaction parameter between the two components of a mixture. The final goal of this research is (1) to evaluate the potential of predictability of theories used to compute fundamental quantities used in thermodynamic models such as molar volumes, and (2) to constrain as much as possible the binary interaction parameters so that the step of model adjustment to experimental solubility data is no longer needed.

**Methods:** Experimental data are collected on various binary systems involving Titan's fluids (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, N<sub>2</sub>) and possible solids (C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, nC<sub>4</sub>H<sub>10</sub>, C<sub>6</sub>H<sub>6</sub>, ...) from the DDBST<sup>1</sup> thermodynamic database. The solubility ( $x_i$ ) of a solid in a liquid is given by the following formula [7]:

$$\ln(x_i\gamma_i) = -\Delta H_{m,i}/RT (1 - T/T_{m,i}) + \Delta C_{p,m,i}/R (T_{m,i}/T - 1) - \Delta C_{p,m,i}/R \ln(T_{m,i}/T) \quad (1)$$

Where  $\Delta H_{m,i}$ ,  $\Delta C_{p,m,i}$  and  $T_{m,i}$  are the enthalpy change, heat capacity change and the temperature of melting of the solid. In most papers only the first part of the equation is used (enthalpy and temperature of fusion can be easily found in handbooks of chemistry [8]) and the heat capacity terms are usually neglected. In this work, we consider all these three terms of Equation 1.

The activity coefficient  $\gamma_i$  of the solute in Equation 1 is computed from a modified RST equation taking into account both the combinatorial (entropic) and residual (enthalpic) parts of the coefficient. The residual term is the one of the RST:

$$\ln(\gamma_i) = \ln(\gamma_i)_{\text{comb}} + \ln(\gamma_i)_{\text{res}} \quad (2)$$

$$\ln(\gamma_i)_{\text{comb}} = \ln(\phi_i/x_i) - (\phi_i/x_i) + 1 \quad (3)$$

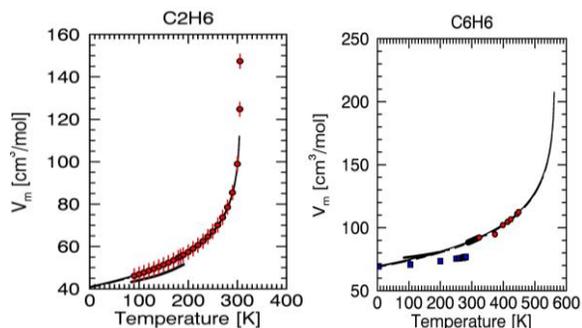
$$\ln(\gamma_i)_{\text{res}} = V_{m,i} \phi_j [(\delta_i - \delta_j)^2 + 2 I_{ij} \delta_i \delta_j] / RT \quad (4)$$

Where  $V_{m,i}$  is the subcooled saturated molar volume of the solute  $i$ ,  $\phi_j$  is the volume fraction of the solvent  $j$  (relying on the molar volume of  $i$  and  $j$ ),  $\delta$ 's are the solubility parameters of each compound and  $I_{ij}$  is the binary interaction parameter. Sources of uncertainty in this model are mostly associated with the estimates of molar volumes and binary interaction parameters (usually set to 0 when unknown, or used as constant with temperature).

#### Estimates of $V_m$ and $I_{ij}$ for the RST model:

*Molar volume estimations.* We used two independent theories to determine the temperature variation of molar volumes: the Rackett equation [7], which provides estimates of the saturated liquid molar volumes (i.e. for  $P = P_{\text{sat}}$ ) from the critical properties, and the Peng-Robinson Equation of State, which determines the molar volumes for a given desired pressure [9]. Figure 1 shows two examples of molar volumes determined from experiments on ethane and benzene, to which are overlaid a set of curves coming from the Rackett equation or the Peng-Robinson EoS. It seems that the Rackett equation is accurate enough to represent the temperature variation of molar volume for these simple components. The Peng-Robinson results are quite close to experiments, which is extremely important in order to be able to predict accurate molar volumes for other P,T conditions (e.g. for any vapor-liquid equilibrium relevant to Titan science).

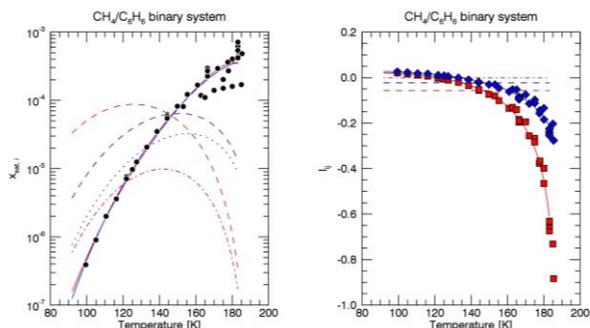
<sup>1</sup> Dortmund Data Bank Software & Separation Technology



**Figure 1:** Examples of the fitting of experimental data for a Titan liquid (ethane) and a Titan solid (benzene) versus temperature. Red circles are data coming from liquid density measurements [13,14]. Blue squares are data coming from crystallography measurement [15]. Solid thin lines are various versions of the Rackett Equation, while the solid bold line is coming from the Peng-Robinson EoS in the liquid stability domain of each compound.

*Binary interaction parameter determination in a binary Solid-Liquid Equilibrium (SLE).* The chosen system for our tests is a methane – benzene Solid-Liquid Equilibrium, which has the advantage of (1) being highly relevant for Titan, and (2) having been studied experimentally from about 100 K to 190 K [10-12]. From the solubility data points, one can estimate the experimental activity coefficient values using Equation 1. From the experimental activity coefficient values and Equation 2-4, one can infer the experimental binary interaction parameters to be fitted to fully constrain the thermodynamic model (Figure 2). We perform the fits using the IDL MPFITFUN package [17], based on a Levenberg-Marquardt chi square minimization. We find that using a constant value for the binary interaction parameter of this system (either 0 or any other value) cannot successfully represent the experimental solubility. However, using a linear relationship based on a solubility parameter ratio between the solute and the solvent seems to represent much better the data.

**Preliminary conclusions:** The RST model used in several studies suffers, as many other thermodynamic models, from the lack of constraints due to the absence of solubility experiments at Titan temperatures, especially for complex molecules. We try to evaluate the accuracy of pure component molar volume predictions and to improve the predictability of solubility of solids in liquids in order to bypass the step of future model adjustment to experiments. Notably, the binary interaction parameters seem to rely on variables specific to the system studied, such as solubility parameters ratios.



**Figure 2: Left)** Solubility of solid benzene in liquid methane at cryogenic temperatures. **Right)** Binary interaction parameter evolution with temperature. Circles and squares are experimental values. Red: the RST model using the Hildebrand solubility parameter. Blue: the RST model using the Hansen Solubility Parameter approach [16]. Dotted curves:  $l_{ij}$  set to 0. Dashed curves:  $l_{ij}$  set to a constant. Dash-dot curves:  $l_{ij}$  set to a constant from literature. Solid curves: our fits using a linear relationship between  $l_{ij}$  and the  $\delta_2/\delta_1$  ratio.

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