**FITTING NITROGEN SOLUBILITY LAB DATA FOR MODELING TITAN'S LAKES AND SEAS** Gigja Hollyday[1], Michael J. Malaska[2], Robert Hodyss[2], Karl Mitchell[2], Jonathan I. Lunine[3], Alex G. Hayes[3], Jason Hofgartner[2], Ralph Lorenz[4]. [1]University of Redlands, Redlands, CA. [2]Jet Propulsion Laboratory / California Institute of Technology, Pasadena, CA. [3]Cornell University, Ithaca, NY, [4]Applied Physics Lab, The Johns Hopkins University, Laurel MD. (Gigja_Hollyday@redlands.edu)

Introduction: Titan's surface-atmosphere system is mostly dry but large portions of the northern hemisphere, and lesser portions of the south, are covered by liquids. Radar and near-infrared data sets show that these bodies of liquid are primarily methane and ethane [1,2,3], and it has been known for over 30 years [4,5] that the high nitrogen pressure in the atmosphere requires that it be a substantial, dissolved third component (figure 1). However, available chemical and chemical engineering data are sparse and uneven in quality, so that up to now models of the behavior of these ternary liquids on the surface have been limited by the accuracy of the lab data. Malaska et al (this conf.) present new laboratory measurements, and here we compare those with the literature data and develop heuristic models of utility in applying the lab data to liquids of varying composition on Titan's surface.
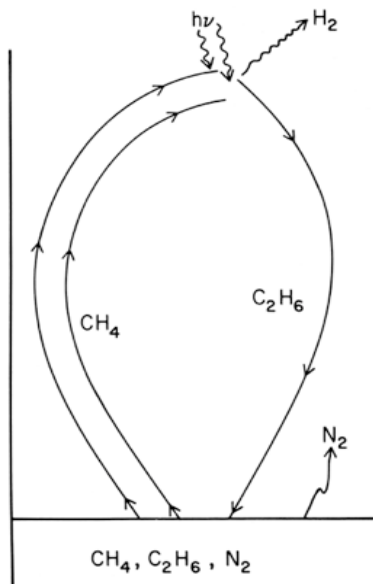
Figure 1. Progressive conversion of methane to ethane drives nitrogen out of surface liquids over long time periods. Adapted from [4].

Henry's Law and the ternary system: We use a Henry's law approach to correlating data sets found in the refereed literature and comparing with more recent laboratory data. Doing so allows our results to be used in evolution models of Titan where the nitrogen partial pressure in the atmosphere is not constant. Calculating the Henry's law constants K_h [p/x] for nitrogen in methane, we digitized pressure-temperature (P-T) data for seven nitrogen compositions (mole fractions of 0.75,

0.604, 0.5, 0.262, 0.197, 0.128, and 0.037) from [6]. We made a fit for each of the P-T curves and chose the temperature value from each curve that corresponded to a pressure of 1.5 bar, the nitrogen partial pressure at Titan's surface (within 5%, the total pressure).

Let the indices 1=CH_4, 2 = N_2, and 3 = C_2H_6. The Henry's law constant for N_2 in CH_4, H_{13}, was calculated for those temperatures and compositions at 1.5 bar:

$$K_{12}(T) = 1.5bars/x_{12}$$

where x_{12} is the mole fraction of N_2 in pure CH_4.

Figure 2 shows the Henry's Law coefficient K_h for methane plotted against the corresponding temperature. The literature data can be well fitted by a linear relationship of K with T ($K_{12} = 0.524*T - 42.398$), with the exception of the highest temperature point (corresponding to a nitrogen composition of 0.037), which seems quite anomalous. The recently obtained data in our laboratories fit the linear relationship $K_{12} = 0.6505*T-52.006$. The linear positive correlation between Henry's law constant and temperature implies that as temperature increases, at a constant pressure of 1.5 bar, the solubility of nitrogen in methane decreases.

Calculating the Henry's law constants for nitrogen in ethane, we used pressure-composition (P-x) data from two different sources, [7,8]. The first of these [7] had pressure data for six nitrogen compositions at 90.69 K, while [8] had two nitrogen compositions at 92.8 K. We fitted the P-x data and chose the two compositions that corresponded to a pressure within 0.003 bar of 1.5 bar. The corresponding Henry's law constants

$$K_{32}(T) = 1.5bars/x_{32} \qquad (1)$$

are plotted versus temperatures in figure 3.

Implications:
For pure methane as the solvent, the published laboratory data we have studied [6] agrees in the slope with the recent experiments of Malaska et al. (this conf.), that is, both show a decreasing solubility of molecular nitrogen in methane at higher temperatures. However the prior data show lower Henry's law coefficients (higher solubility of nitrogen) than the more recent laboratory measurements. (At the lowest temperature, the coefficient is roughly the saturation vapor pressure

of pure N_2, emphasizing that this is not a dilute solution to which Henry's law properly applies).

Pure ethane, on the other hand, behaves very differently in the new experiments relative to published data. While the latter [7, 8] shows increasing solubility with increasing temperature, the more recent data suggests a decreasing solubility with increasing temperature (Figure 3). The recent laboratory measurements also suggest a non-linear change in the Henry's Law coefficient K_h for ethane, specifically, at higher temperatures the change in the amount of dissolved nitrogen decreases less than at lower temperatures.
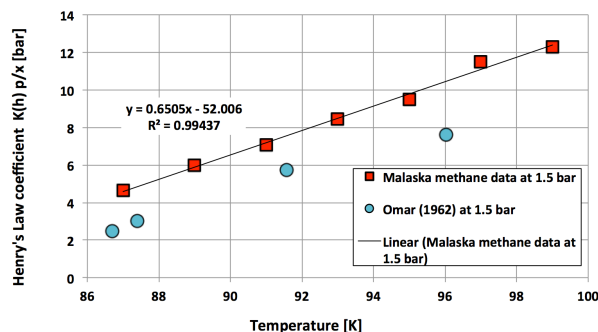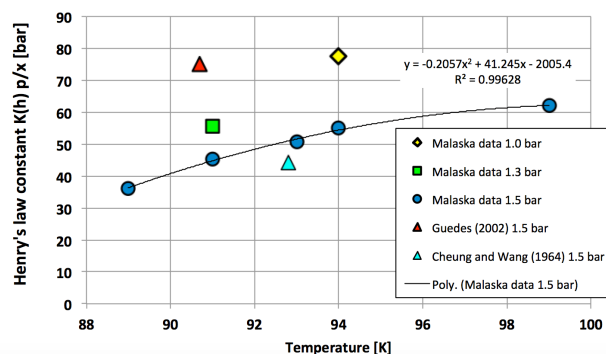

Figure 2. Henry's law fits for nitrogen in methane at 1.5 bar nitrogen pressure from Omar (1962) compared to data from Malaska et al. (this conference)

Because solubility of gases in liquids depends on solute-solvent differences in both enthalpic and entropic terms, it is difficult to predict *a priori* what the temperature dependence of the solubility will be in a given solute-solvent pair. However, given the hydrophobic character of methane and ethane, it seems likely that both should behave roughly similarly as solvents. Both methane and ethane are nonpolar alkanes, and nitrogen is itself nonpolar. Due the larger interaction surfaces of ethane molecules compared to methane, the intermolecular forces may prevent nitrogen from interacting with the solvent to a greater extent in ethane than in methane. The implication is decreased dissolution of nitrogen in ethane compared with methane as solvent.

A preliminary analysis of laboratory data collected at varying pressures suggests that they do not behave as predicted by Henry's Law. The derived Henry's Law coefficients appear have a higher order pressure term (1.0 and 1.3 bar data in Figure 3), and while the data can be fitted in this way, it is difficult to connect this to a physical model of solvent solute interaction.

The non-Henry's law behavior with pressure and the curvature in the Henry's law coefficient with temperature for the ethane-nitrogen binary raise the issue of how to compute the solubility of nitrogen in a ternary solution. For an ideal solution one sums the logarithms of Henry's law coefficients weighted by the mole fractions. In the present case, one should include

a nonideal mixing term $a_{13} x_1 x_3$ whose coefficient expresses the differences in force laws between solvent-solvent and solvent-solute molecular interactions.

Figure 3. Henry's law fits for nitrogen in ethane at 1.5 bar nitrogen pressure from two data sources compared to preliminary data from Malaska et al.

Plugging in numbers for ethane and methane suggest that this term can be comparable to the ideal mixing terms, therefore its inclusion is merited in any predictive equations for the ternary mixture that would be used over a large temperature range.

Conclusions: Recent laboratory measurements of the solubility of nitrogen in ethane and methane suggest deviations from simple Henry's Law approaches. In both methane and ethane, more nitrogen dissolves at lower temperatures. However, the amount of nitrogen that dissolves in methane at lower temperatures is significantly higher than that for ethane at the same low temperatures. The observed non-ideal behavior suggests that more complex models be applied to fitting the data for predictive purposes. Work in progress on models for mixed methane-ethane-nitrogen systems at Titan-relevant pressures and temperatures will be relevant to the behavior of submersible vehicles that someday may be deployed in the Titan seas [9].

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