

PREPARING SOLUBILITY DATA FOR USE BY THE GAS PROCESSING INDUSTRY: ➔ UPDATING KEY RESOURCES

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Mapping Midstream's Future
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Background

- GPA sponsored a number of projects for the collection of VLE and LLE data to describe solubilities of interest to gas processors:
 - Methanol in natural gas and liquid phases
 - CO₂ and H₂S in TEG and EG
 - Hydrocarbons (BTEX) in Amines & Glycols
- **GPSA Engineering Data Book (EDB)**
 - These topics in EDB have not been updated to the most recent data

Background

- **This project:** create models, graphs, etc., as updated content for EDB, and make the data readily usable to GPA members
 - Projects 975-5, 975-7, 975-8
- This work focuses on **simple, generalized** representations of data
 - Use for quick process calculations

Summary

- Topics will be covered separately
 - Solubility of methanol in natural gas and liquids
 - CO₂ and H₂S solubility in glycols
 - Hydrocarbon solubility in amines & glycols
- To Include
 - Review of current EDB (12th) content
 - Treatment of new data
 - Using the information
- *Not all is covered: The paper available on-line*

Solubility: What does it mean?

- Concentration, at specified conditions of equilibrium, of a solute dissolved in a solvent.
- In gas processing:
 - Concentration of a solute in a gas in equilibrium with a liquid phase
 - Concentration of a light solute in a liquid in equilibrium with a gas phase
 - Concentration of a solute in a liquid in equilibrium with another liquid phase
- Always refers to an equilibrium condition

Approach

1. Use common terminology and units for expressing solubility concentrations
2. When feasible use same formats as in existing EDB content
3. When appropriate, create a mathematical model of data. If not, create a graph and/or table.
 - Models should be easy to use (not EOS for simulation software)

Approach

- 4. Generalize the data and simplify
 - Ignore minor variables
 - Group data that are similar

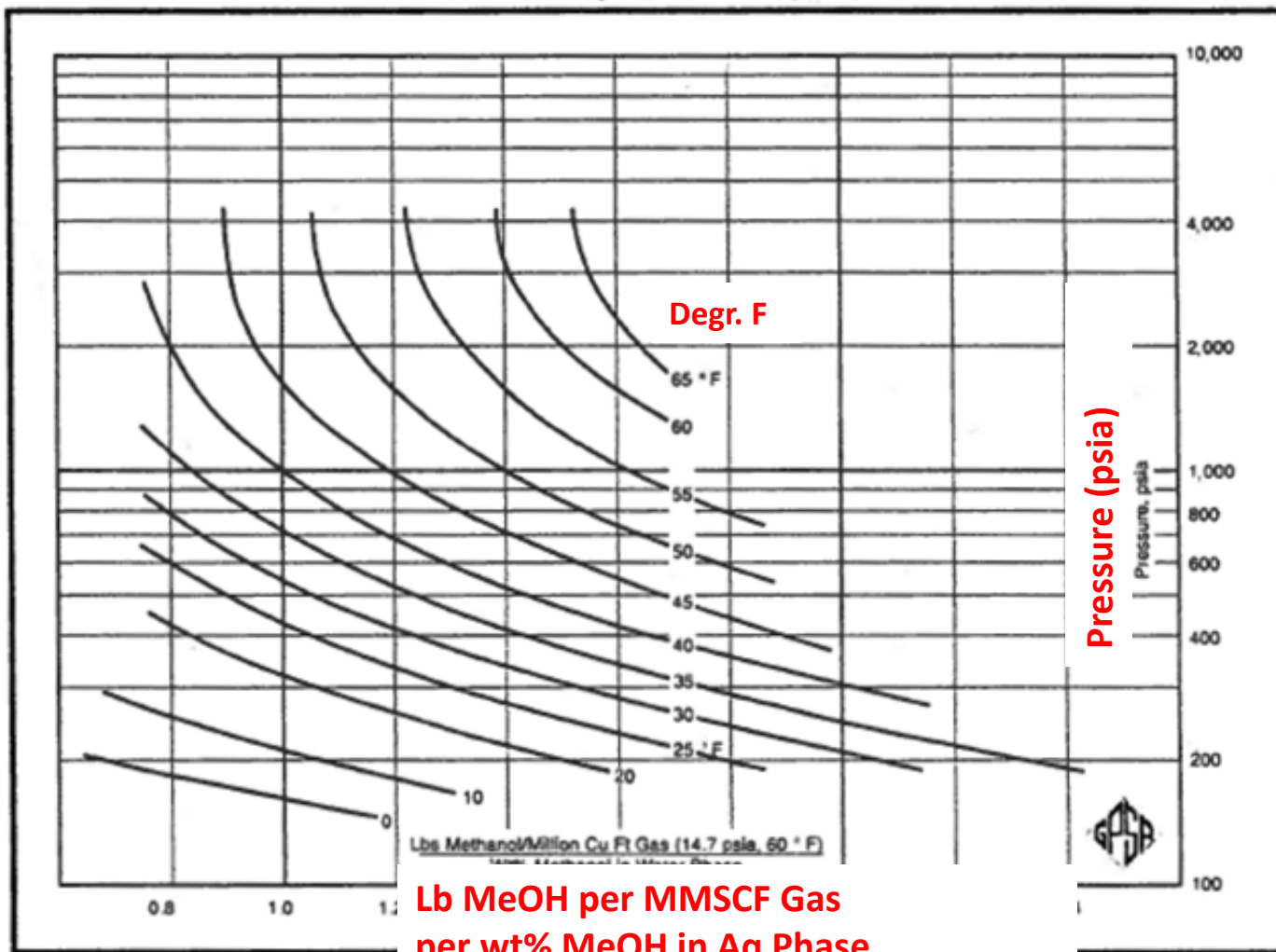
Solubility of methanol in natural gas and HC liquids: GPA Project 975-7

Importance of Data

- Methanol used in hydrate inhibition, dehydration, sweetening
- In Hydrate inhibition:
 - Predict loss of injected methanol in natural gas phase
 - Predict loss of injected methanol in liquid hydrocarbon phase (if present)
 - ➔ Material balance calculations used to predict methanol injection rate required to prevent hydrates

FIG. 20-65

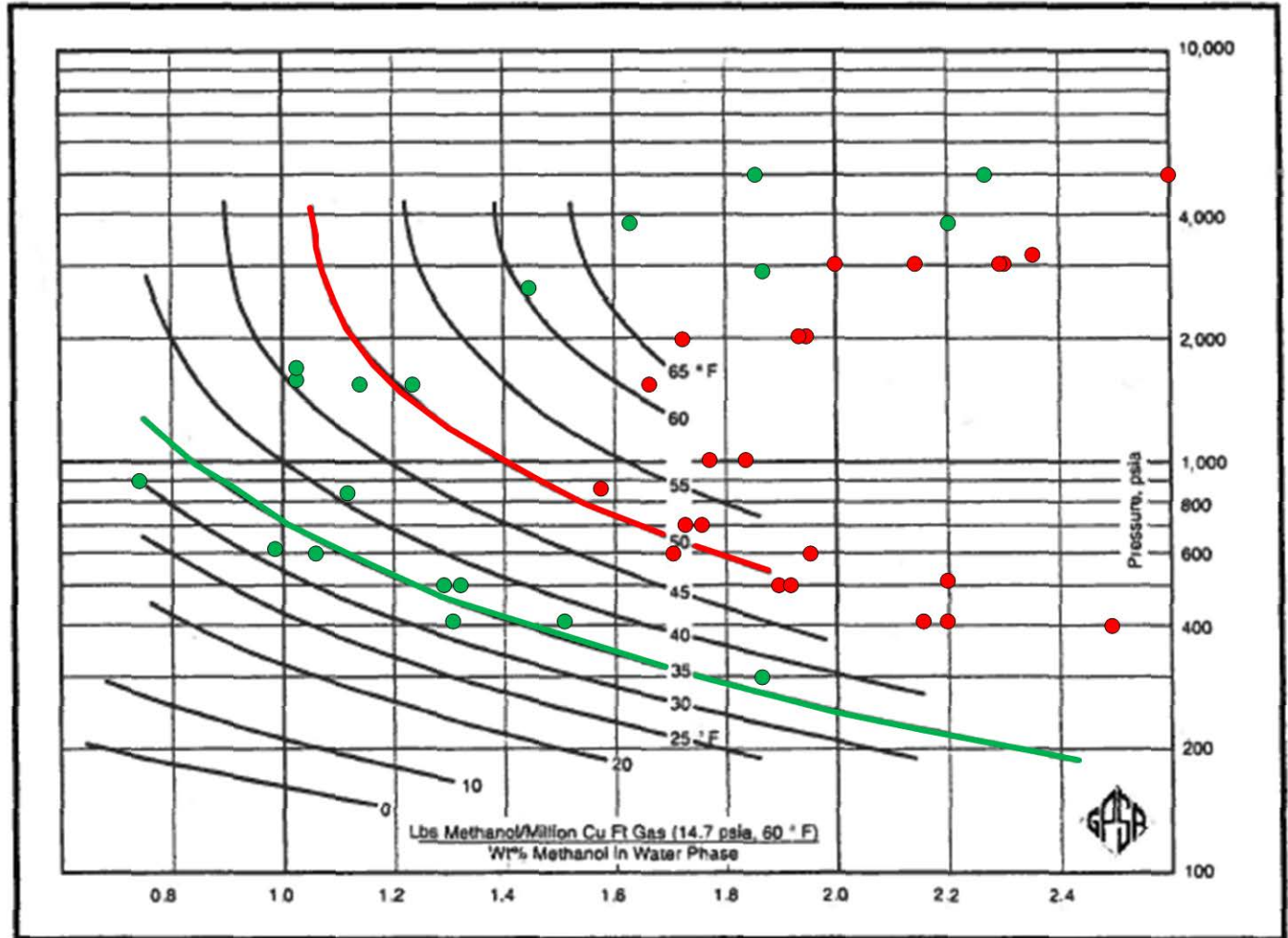
Ratio of Methanol Vapor Composition to Methanol Liquid Composition



Solubility of Methanol in the Natural Gas Phase.
EDB Graph (12th)

FIG. 20-65

Ratio of Methanol Vapor Composition to Methanol Liquid Composition



*Compare with
new data.*

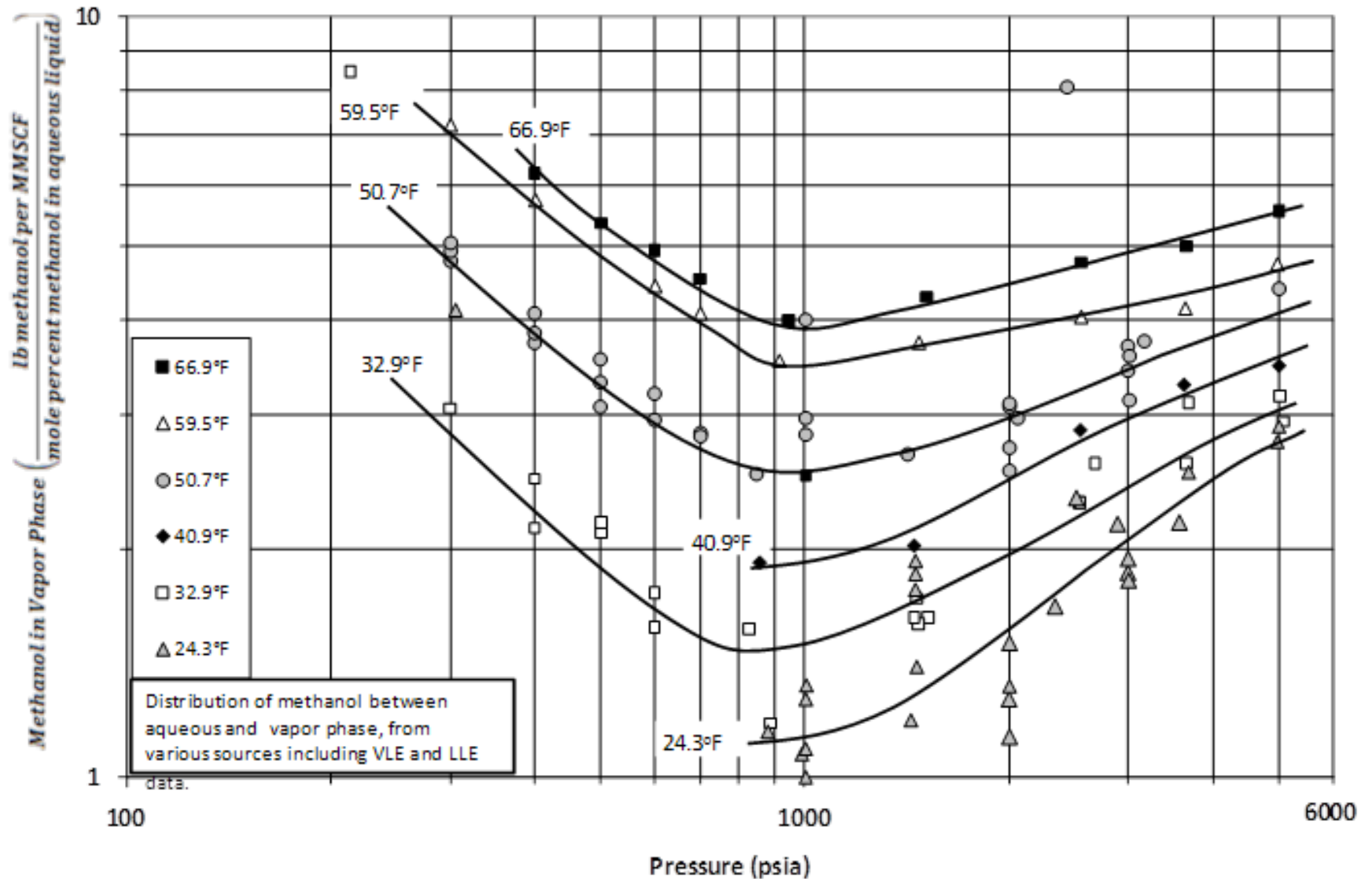
Red & Green
lines are traces
of current
figure 20-65.
Red and Green
Points are
expt'l data

Solubility of methanol in natural gas: *Treatment of new data*



- Variables:
 - Methanol content of aqueous phase
 - Temperature
 - Pressure
- Consistent simple model not developed
- Conclusion:
 - Produce update of EDB Figure 20-65

Figure 1. Solubility of Methanol in the Vapor Phase.

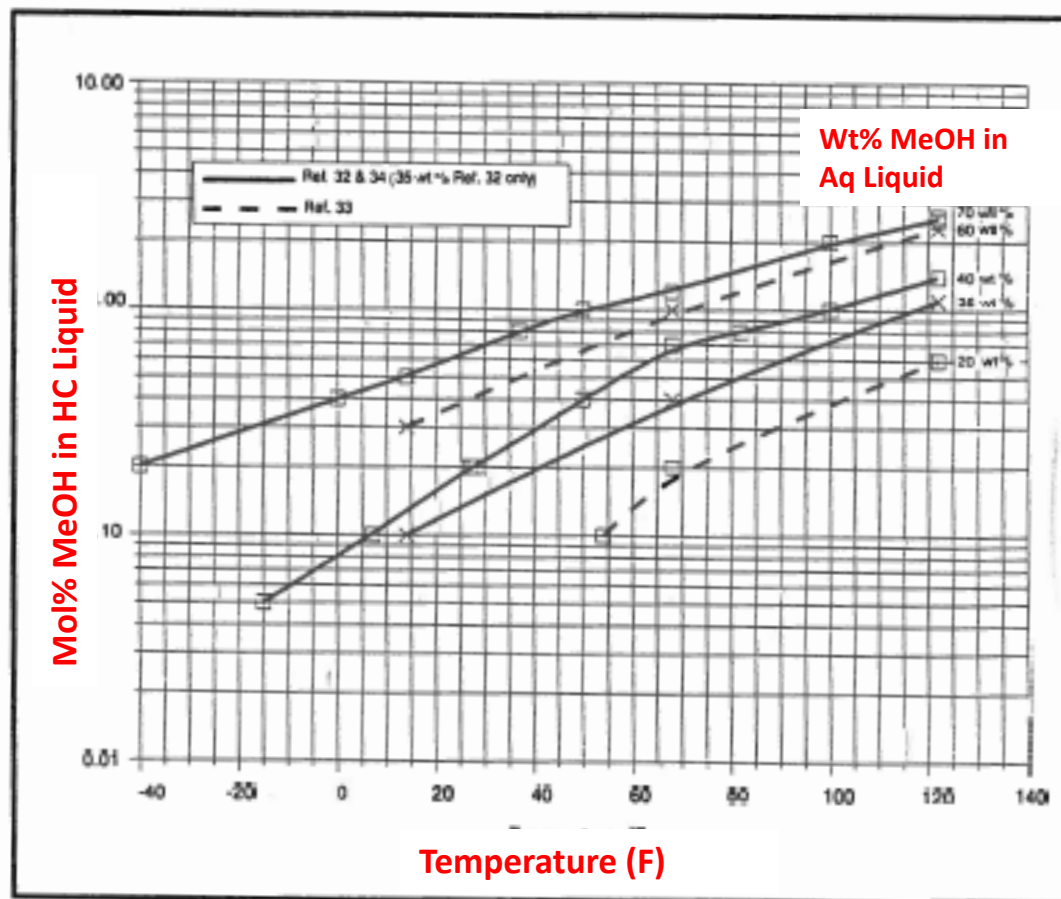


Solubility of methanol in hydrocarbon liquids (975-7)



FIG. 20-66

Solubility of Methanol in Paraffinic Hydrocarbons^{32, 33, 34}
vs. Temperature at Various Methanol Concentrations



Solubility of methanol in hydrocarbon liquids: *Treatment of Data*

- Variables:
 - Methanol content of aqueous phase
 - Temperature
 - Composition of HC liquid phase
 - Pressure – small impact (ignored)
- Express in terms of distribution ratio:

$$\text{Distribution Ratio} = \frac{\text{mole fraction MeOH in aqueous phase}}{\text{mole fraction MeOH in hydrocarbon phase}}$$

Solubility of methanol in hydrocarbon liquids: *Treatment of Data*

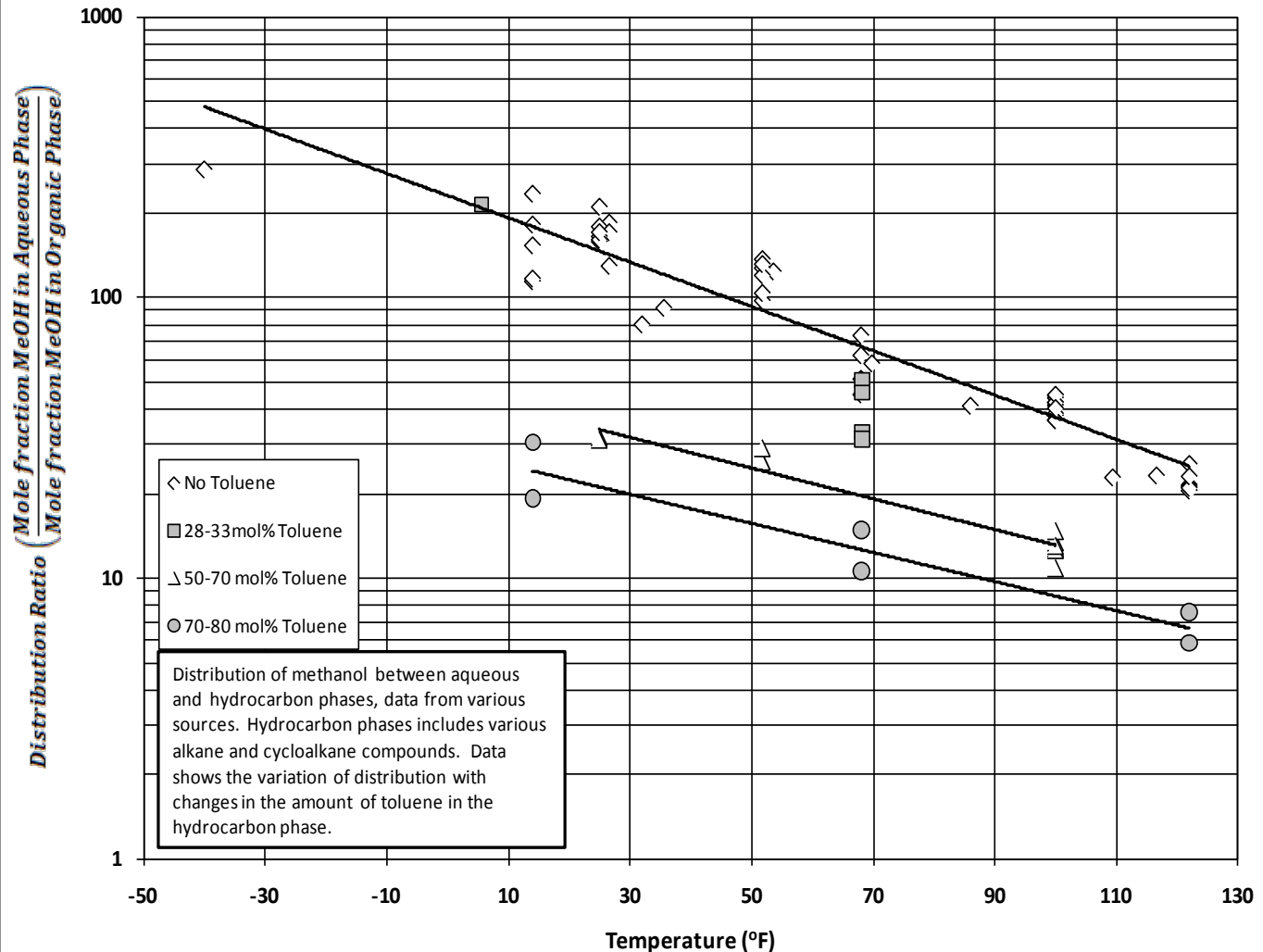
Liquid hydrocarbon phase composition

- Typical hydrocarbon components had minor effect on solubility
- Toluene had a significant effect
 - Implies that all aromatics will probably be significant

Methanol solubility in liquid hydrocarbons: Proposed representation of data.

Groups all hydrocarbons except toluene (aromatics).

Figure 2. Liquid-Liquid Methanol Distribution Ratios.



Solubility of CO₂ and H₂S in TEG & EG: Project 975-8

Importance of Data

- H₂S and CO₂ in gases being dehydrated can dissolve in the solvent under pressure and then be released to the gas phase during flash and regeneration steps
- Important for a few reasons:
 - Product Quality
 - Environmental
 - Safety
 - Design of equipment (e.g., flash drum)

FIG. 20-76

Solubility of H₂S and CO₂ in Triethylene Glycol vs. Temperature and Partial Pressure

Current EDB Content.

Solubility in TEG as function of temperature and H₂S or CO₂ partial pressure

Solubility defined in terms of std vol of gas per gallon solvent

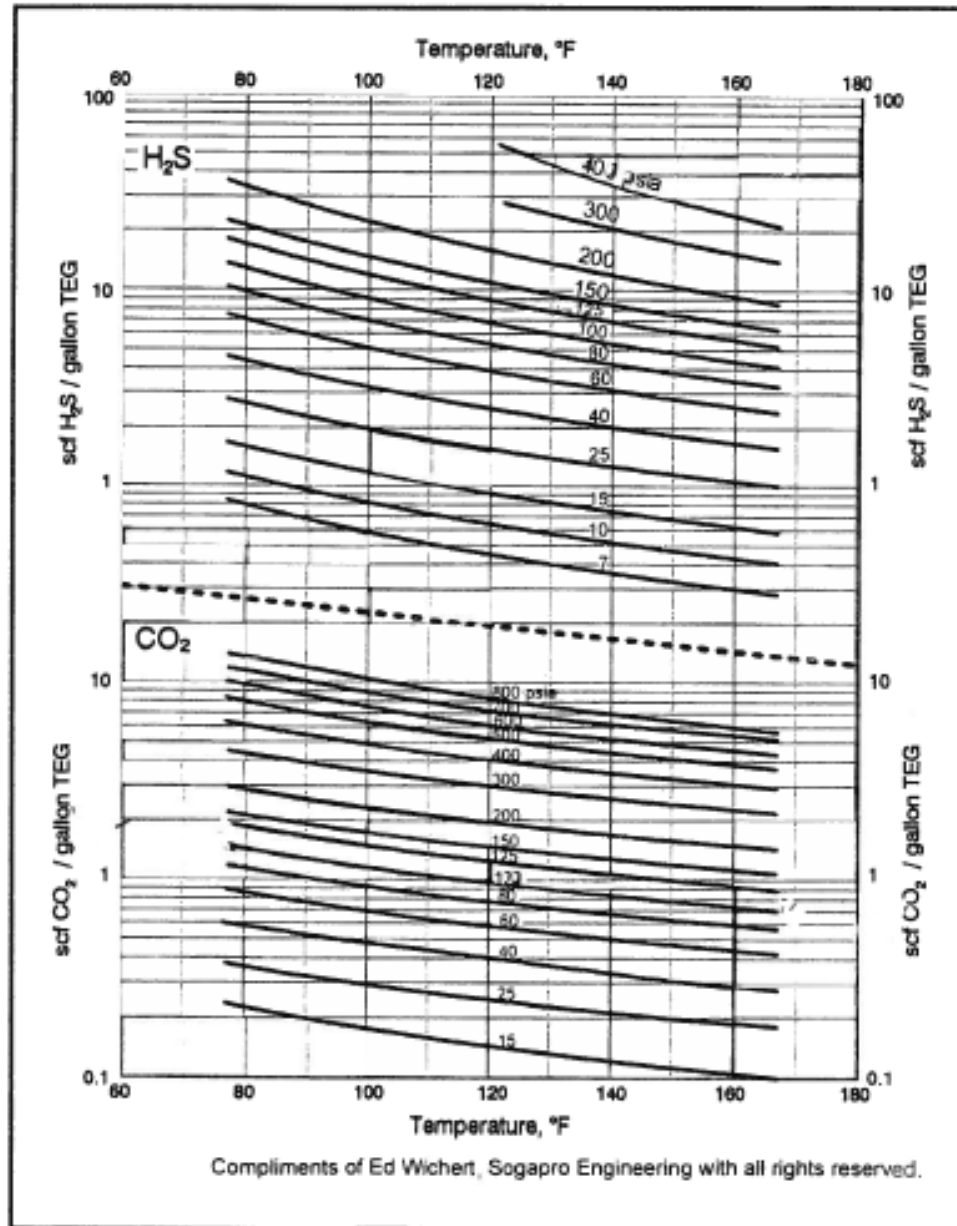
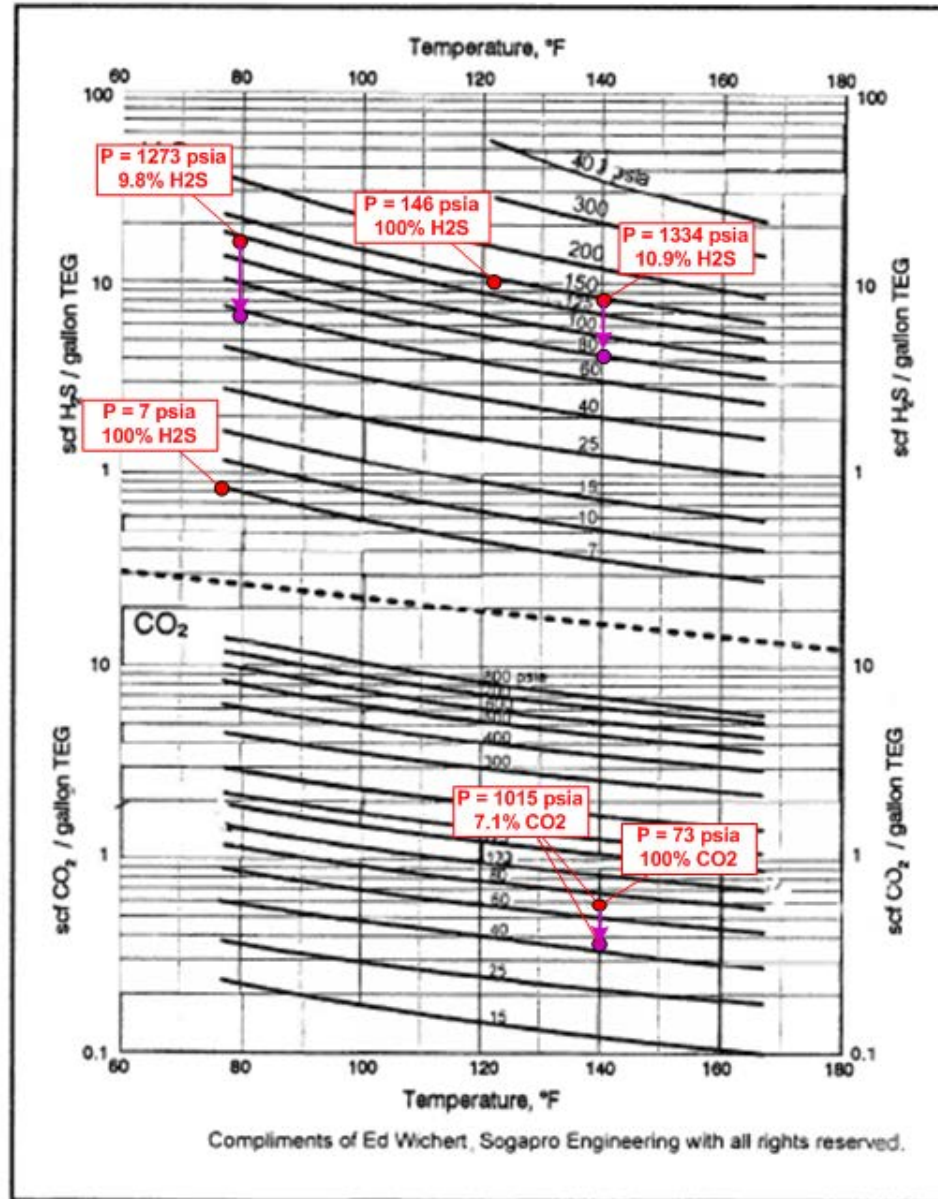


FIG. 20-76

Solubility of H₂S and CO₂ in Triethylene Glycol vs. Temperature and Partial Pressure



Compare with new data.

Purple points are expt'l data (scf / gallon) at the T & P_i of the red data point.

Solubility of CO₂ and H₂S in TEG & EG: *Treatment of Data*

- Modeling *versus* graphing
 - The new data was not amenable to parametric graphing
 - Various mathematic models were attempted
- Final model based on one used by source data authors

Solubility of CO₂ and H₂S in TEG & EG: *Treatment of Data*

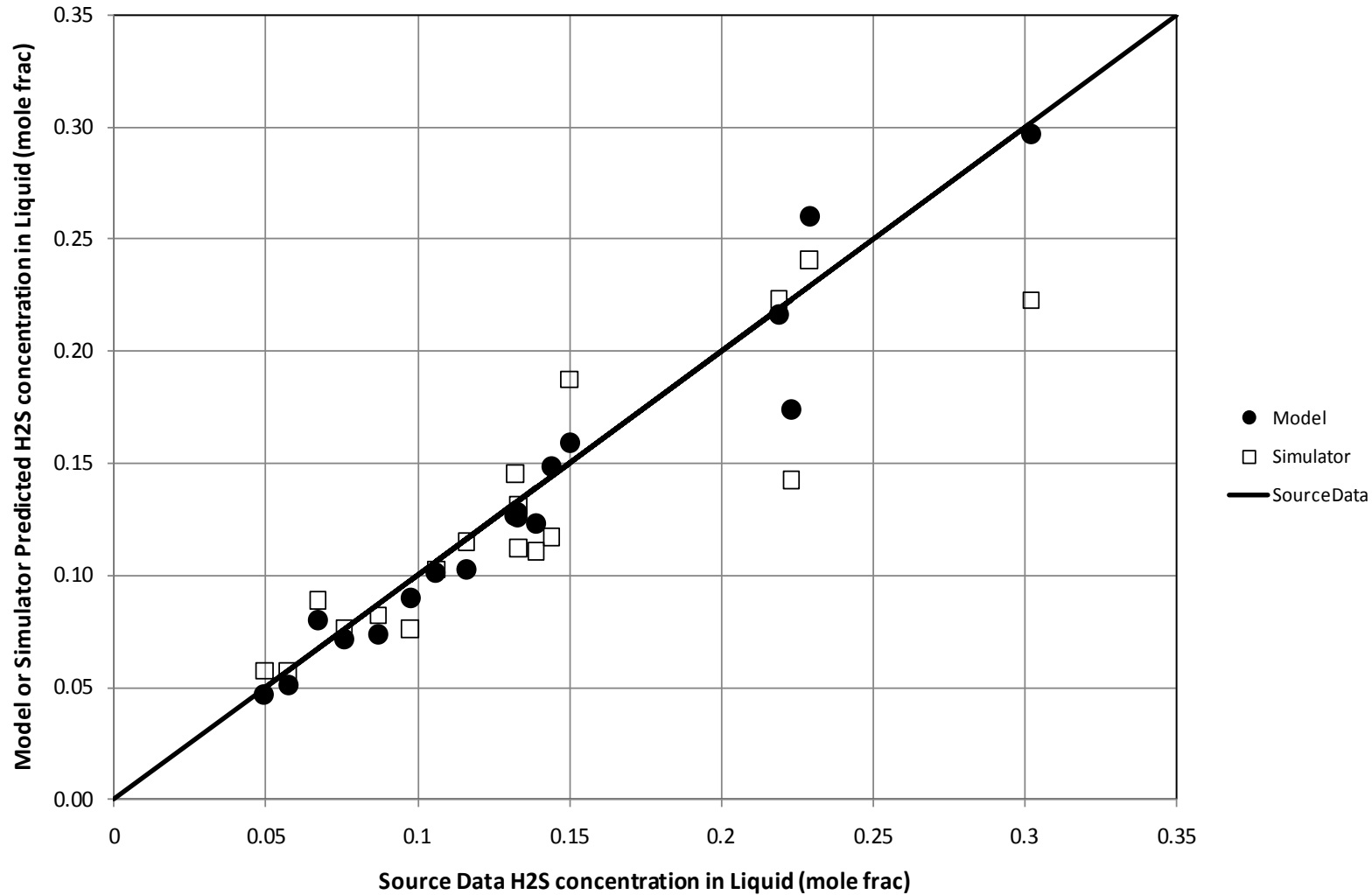
$$x_i = \frac{P_i}{\exp \left[A + B \left(\frac{1}{T} - E \right) + C x_{H_2O} + D \frac{P}{T} \right]}$$

- P_i is the partial pressure of the acid gas (component i : CO₂ or H₂S)

$$P_i = y_i P$$

- y_i is the mole fraction of acid gas in the vapor phase
 - x_i is the mole fraction of the acid gas in the liquid phase
 - T is the absolute temperature
 - x_{H_2O} is the mole fraction of water in the liquid phase
 - P is the absolute pressure
 - Different A, B, C, D constants for each of the four systems based on data fit
- x_i can be used to calculate the solubility of CO₂ or H₂S in units of std vol of gas per volume of solvent

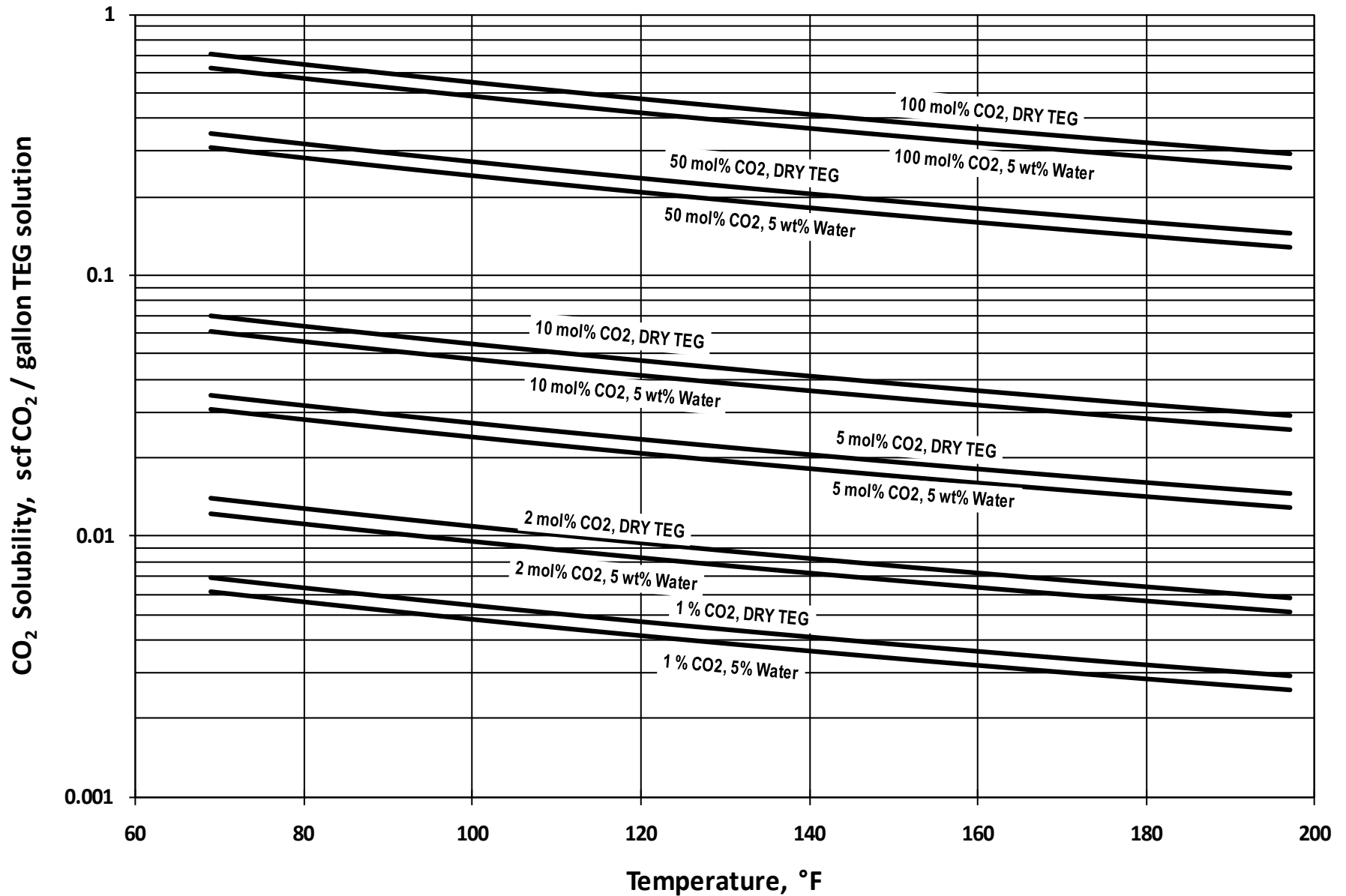
Figure 9. Solubility of H₂S in TEG: Correlation of Reference 2 data with the Model-Generated and Process Simulation Software-Generated Data.



Correlation plot of model to data

Simulation software VLE method: Peng-Robinson

FIGURE 10. Approximate Solubility of CO₂ in Triethylene Glycol at 50 psia vs. Temperature, H₂S Content of Gas Phase, and Water Content of TEG



Solubility of CO₂ and H₂S in TEG & EG

Uses of Data

- Charts and models can be used to **estimate** the equilibrium content of gases in glycols
 - Can be used to estimate the uptake of CO₂ and H₂S in TEG contactor, and the subsequent release to the gas phase in the flash and regeneration
- Can also use as a check of other models (e.g., simulations)

Solubility of Hydrocarbons in Glycols and Amines

- Project 975-5
- Vapor-liquid and liquid-liquid equilibria
- Data collection focused on BTEX compounds, and the differences between similar aromatic and non-aromatics

Solubility of Hydrocarbons in Glycols and Amines

Importance of Data

- Predict hydrocarbon absorption from gas during amine and glycol treating
- Vaporization during flash and regen
 - Equipment design
 - Product loss
 - Environmental (VOC, BTEX)

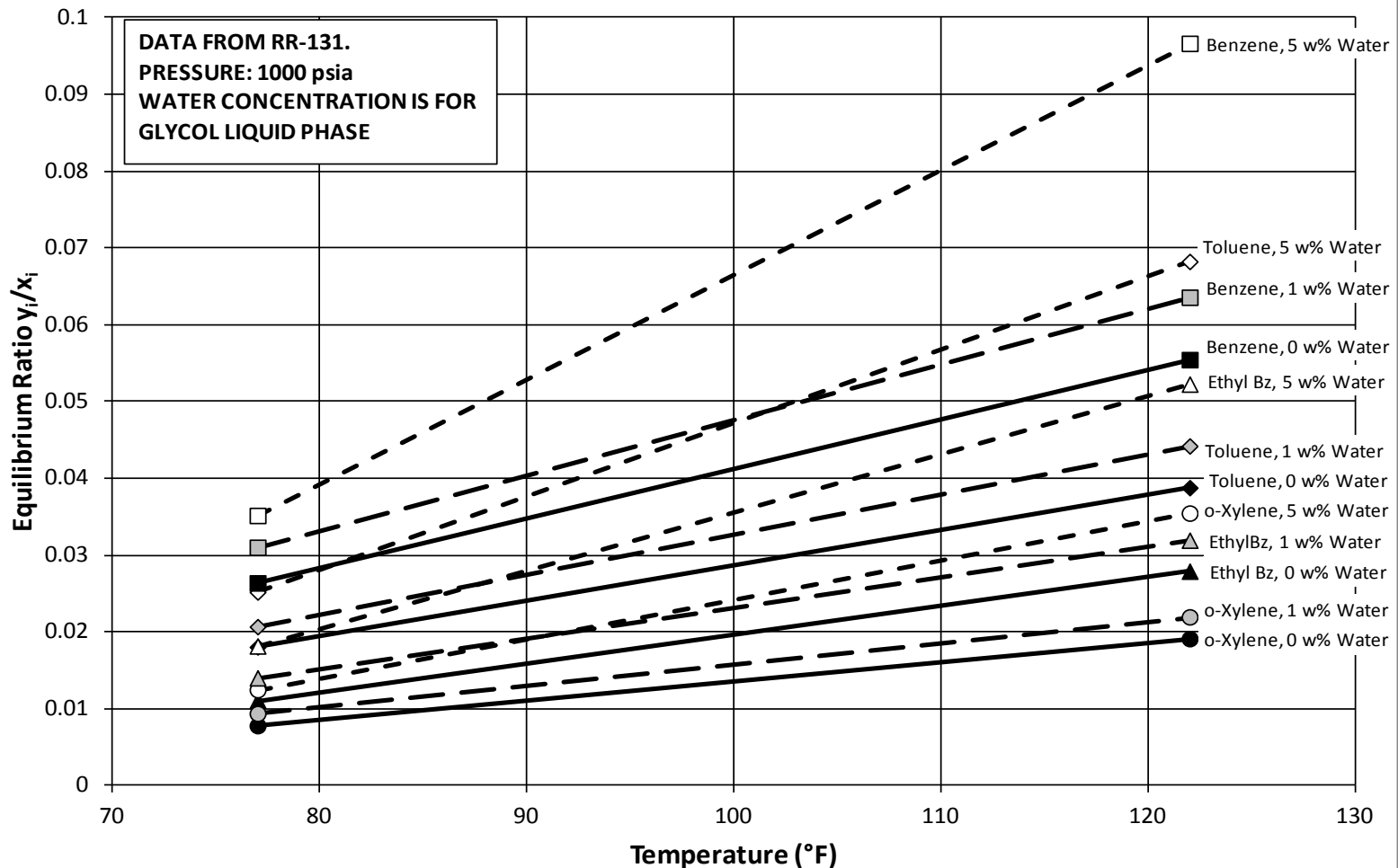
Solubility of Hydrocarbons in Glycols

- *VLE data for BTEX distribution between TEG and gas phase*
 - *Bulk gas phase: methane*
 - *Data taken at conditions typical of TEG dehy regenerator, contactor, and flash drum*
 - *Use equilibrium ratios (K values) to represent data*

$$K_i = y_i / x_i$$

Solubility of Hydrocarbons in Glycols

Figure 4.3. Equilibrium Ratios for BTEX in TEG
Typical Contactor Conditions



Solubility of Hydrocarbons in Amines

- Two data groups:
 - LLE measurements “solubility limit”
 - VLE measurements “subsaturation solubility”
- Majority of data taken via LLE measurements
 - Can be used directly for binary interaction parameters
 - Maybe not as *directly* useful for most gas treating calculations

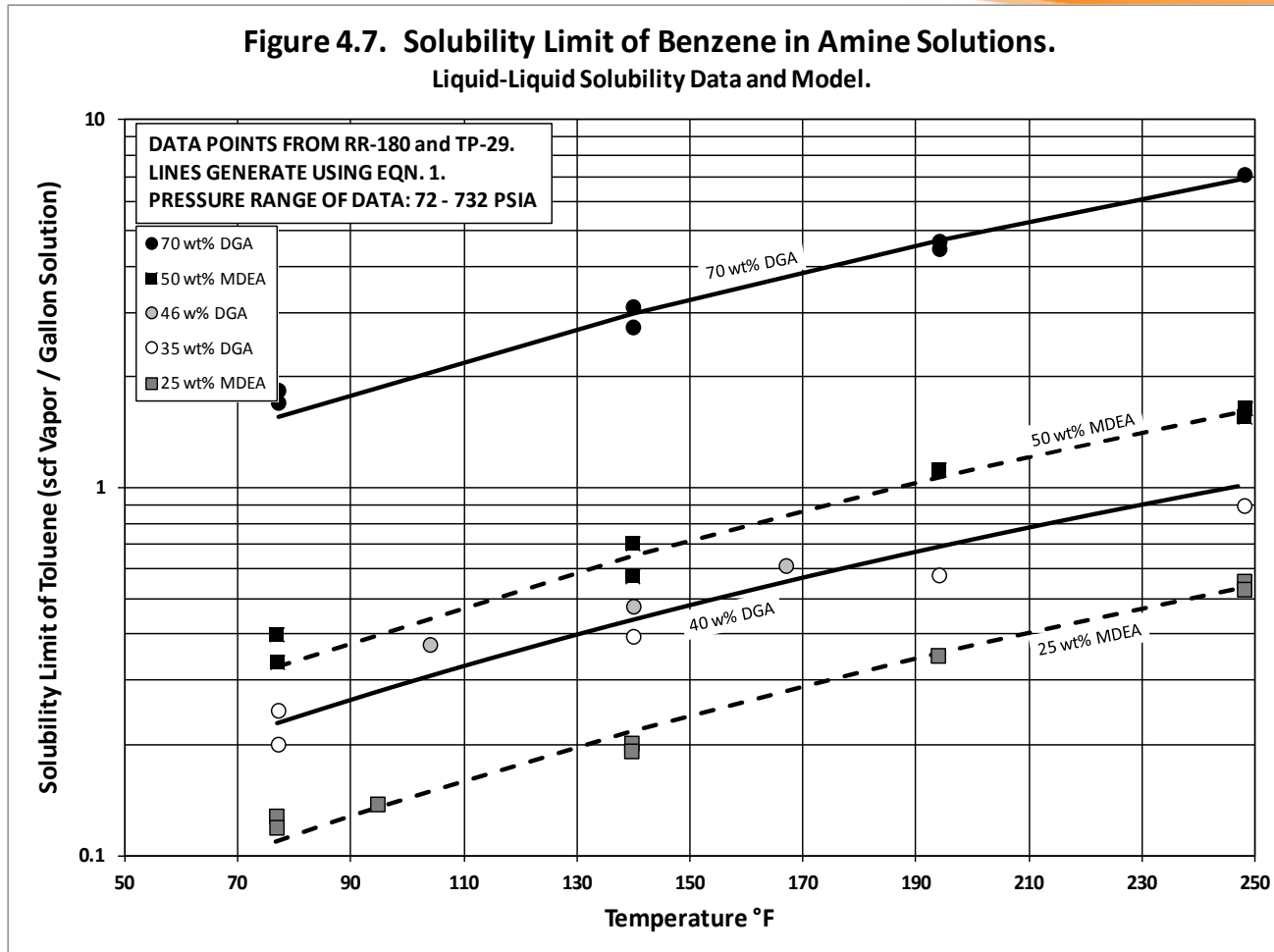
Solubility of Hydrocarbons in Amines

- Solubility limit data (LLE)
 - Solubility in terms of SCF vapor / gallon solution
 - Variables: Temperature, amine, hydrocarbon, water content of amine
 - Little variation with pressure above solubility limit
- Solubility limit data can be modeled

$$\ln S = A + \frac{B}{T} + C * W$$

S is the solubility limit (SCF/gallon sol'n), W is the amine concentration, A, B, C values for each amine – hydrocarbon pair

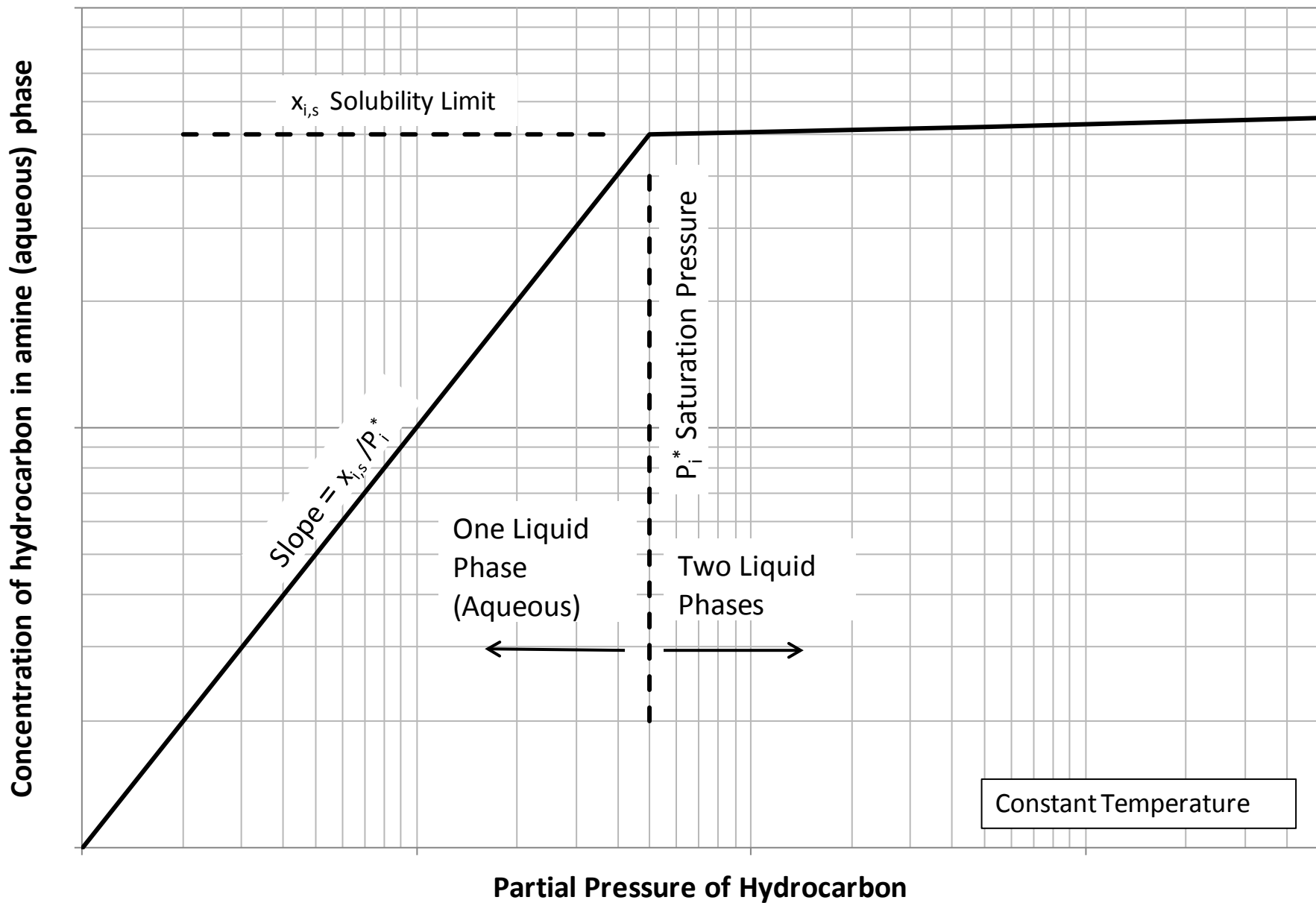
Solubility of Hydrocarbons in Amines



Solubility of Hydrocarbons in Amines

- VLE data (subsaturations)
 - Less data available
 - Represented as equilibrium ratio (K) values
- Rough approximation: base subsaturation solubility on solubility limit data

Figure 16. General Approximation of Hydrocarbon Solubility.



Solubility of Hydrocarbons in Amines

Table 4.3. Experimental K values compared with Estimations from Equation 4.6

Hydrocarbon	Amine Solution	Temperature (F)	Pressure (psia)	K Experimental	K Eq. 4.6
Toluene	50 w% MDEA	140	73	15.6	12.9
Toluene	50 w% MDEA	140	1019	3.9	0.9
Cyclohexane	50 w% MDEA	140	73	316.6	296
Benzene	50 w% MDEA	140	73	19.7	16.9

Conclusions

- See reports (presentation and Research Reports) for:
 - More data and details, graphs
 - Discussion of general trends
- Research reports contain reference for the source data
- Updated content submitted for consideration for next version of EDB