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Methane Hydrate Formation Behavior in the Presence of Selected Amino Acids

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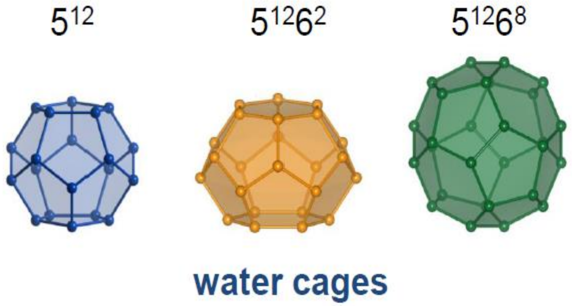
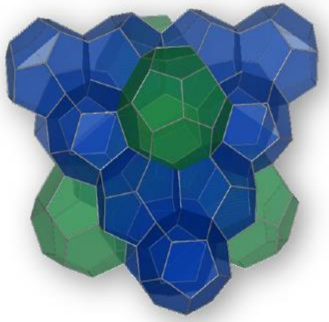
ICCSE 2019

Introduction

What are Gas Hydrate ?

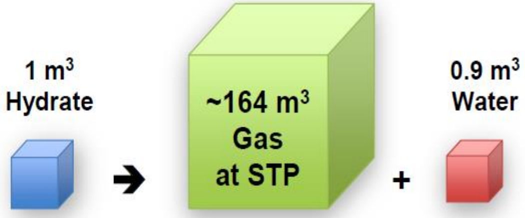
- Ice-like, crystalline structures
- Common hydrate formers: methane, ethane, propane, carbon dioxide, hydrogen sulfide, nitrogen, hydrogen



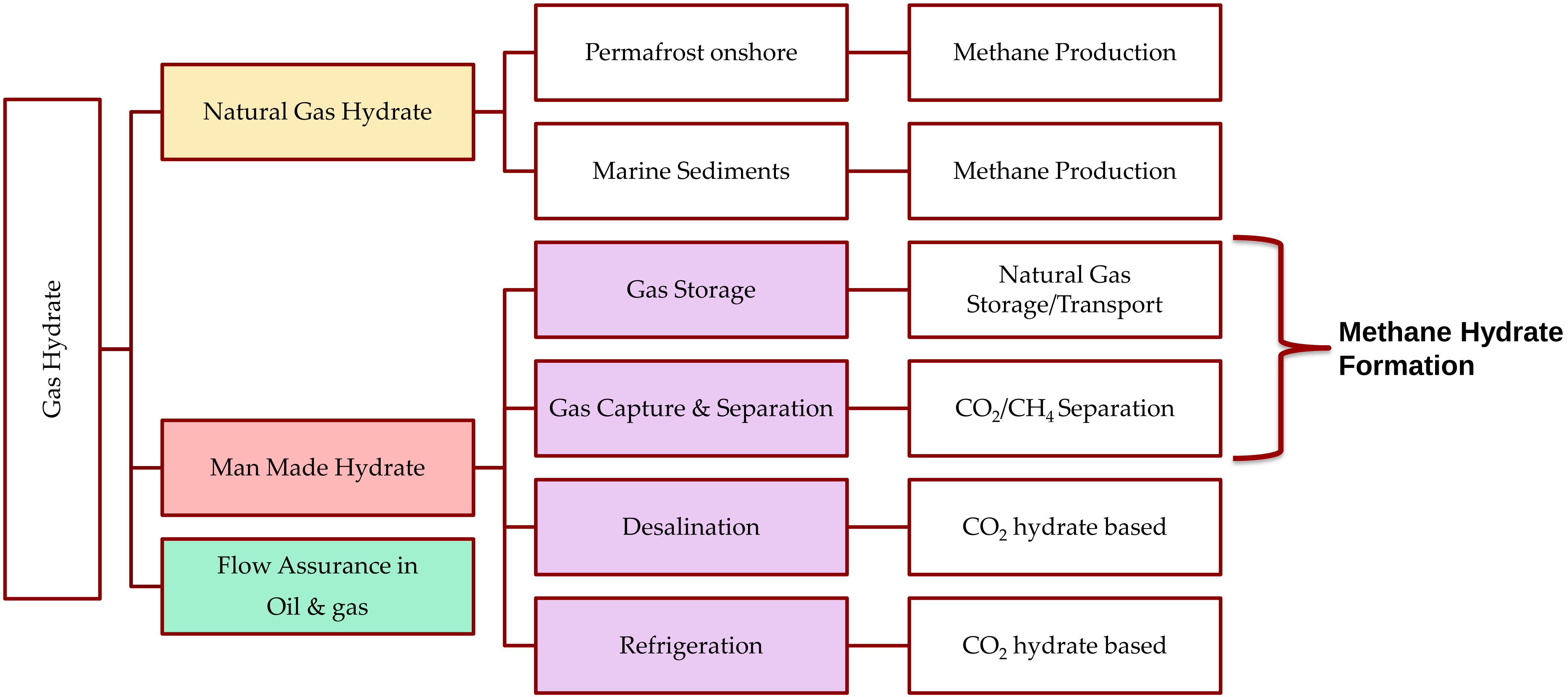


Burning hydrate

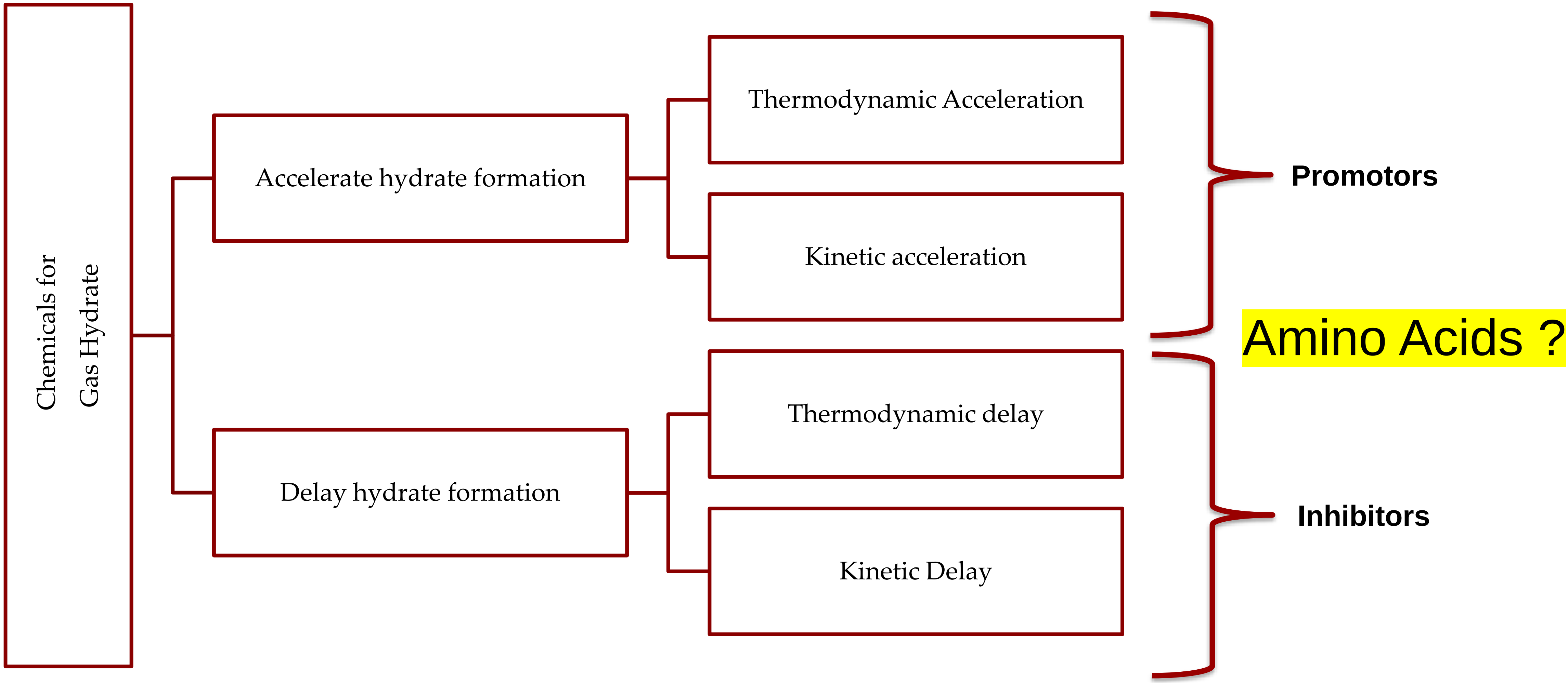
Gas storage capacity in hydrates



Application of Gas Hydrate



Chemicals For Gas Hydrates



Why Amino Acids ?

Available Chemicals					Amino Acids		
Toxic	By product of petroleum	Create foam	Expensive	Large Quantity	Environment Friendly	Non Toxic, Bio degardable	Non Expensive

Objective

- Understand the kinetics of methane hydrate formation
  - In presence of Amino Acids

- Understand the role of Amino Acids
  - Promoter or Inhibitor

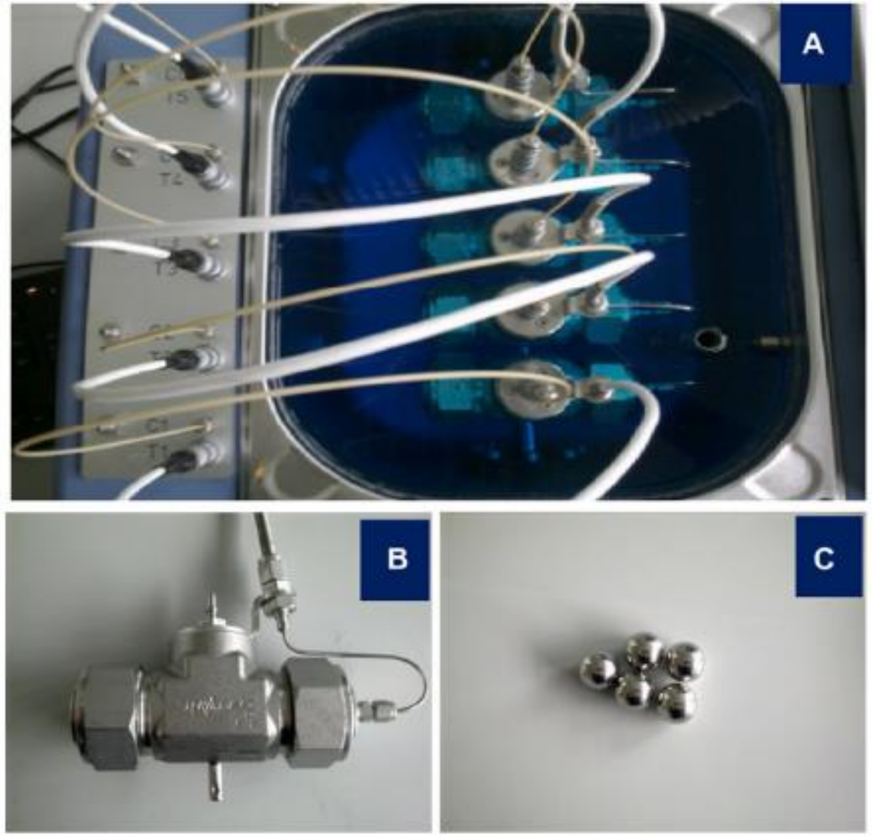
- Explain the mechanism

Selected Amino Acid in this study

#	Name	Side Chain polarity	Side Chain	Hydrophobicity/ Hydropathy Index (Kyte and Doolittle, 1982)
1.1	**L –valine**	Non polar	$-CH(CH_3)_2$	4.2
2.1	**L –methionine**	Non polar	CH_3-S-$(CH_2)_2$	1.9
3.1	**L –histidine**	Basic polar, aromatic side chain	$-CH_2C_3H_3N_2$	-3.2
4.1	**L-arginine**	Basic polar aliphatic side chain	$HN=C(NH_2)$-$NH(-CH_2)_3$	-4.5

Experimental Setup

Rocking Cell (PSL Germany)



- A- Bathtub
- B- High Pressure Cell
- C- Rocking Balls

- Rocking Rate, Rocking Angle
- Volume
- Temperature Ramping, Constant Temperature

Temperature Scheme

Isothermal Experiment
(Fresh & Memory)

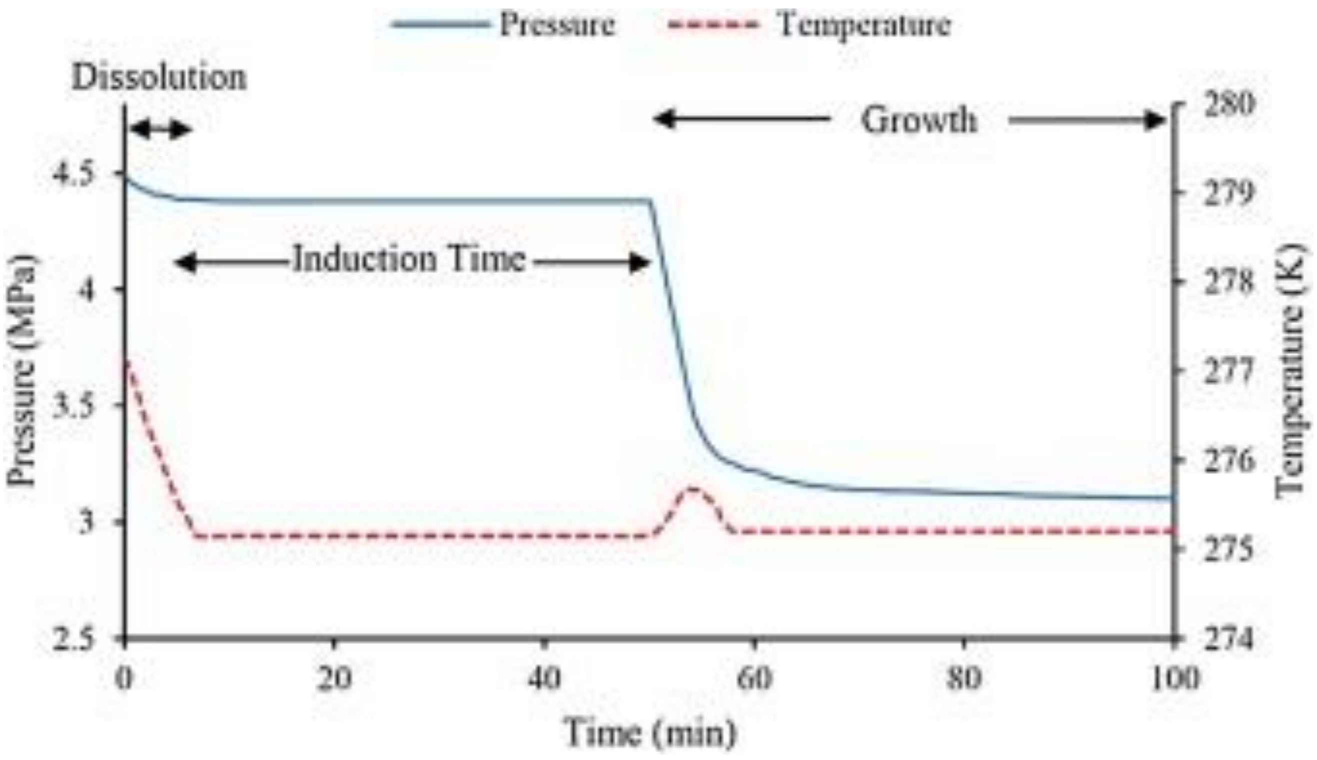
Induction Time (t_o)

Gas Uptake

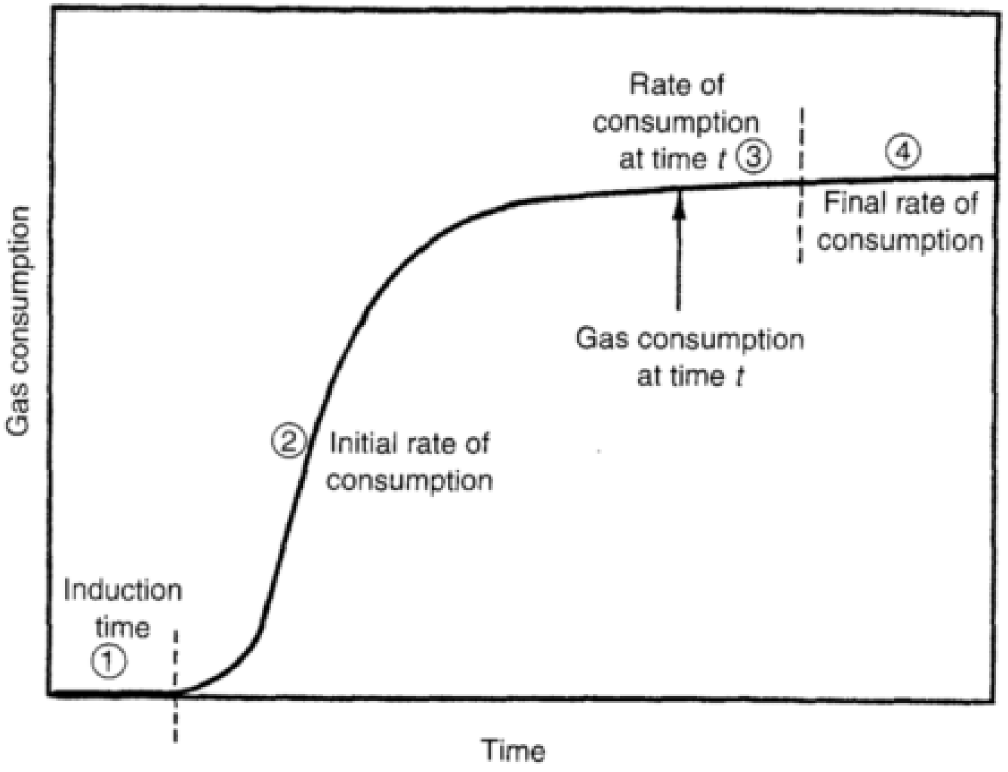
$$uptake = \frac{\Delta n_H^{methane\ gas}}{n_{Sol}}$$

Methodology

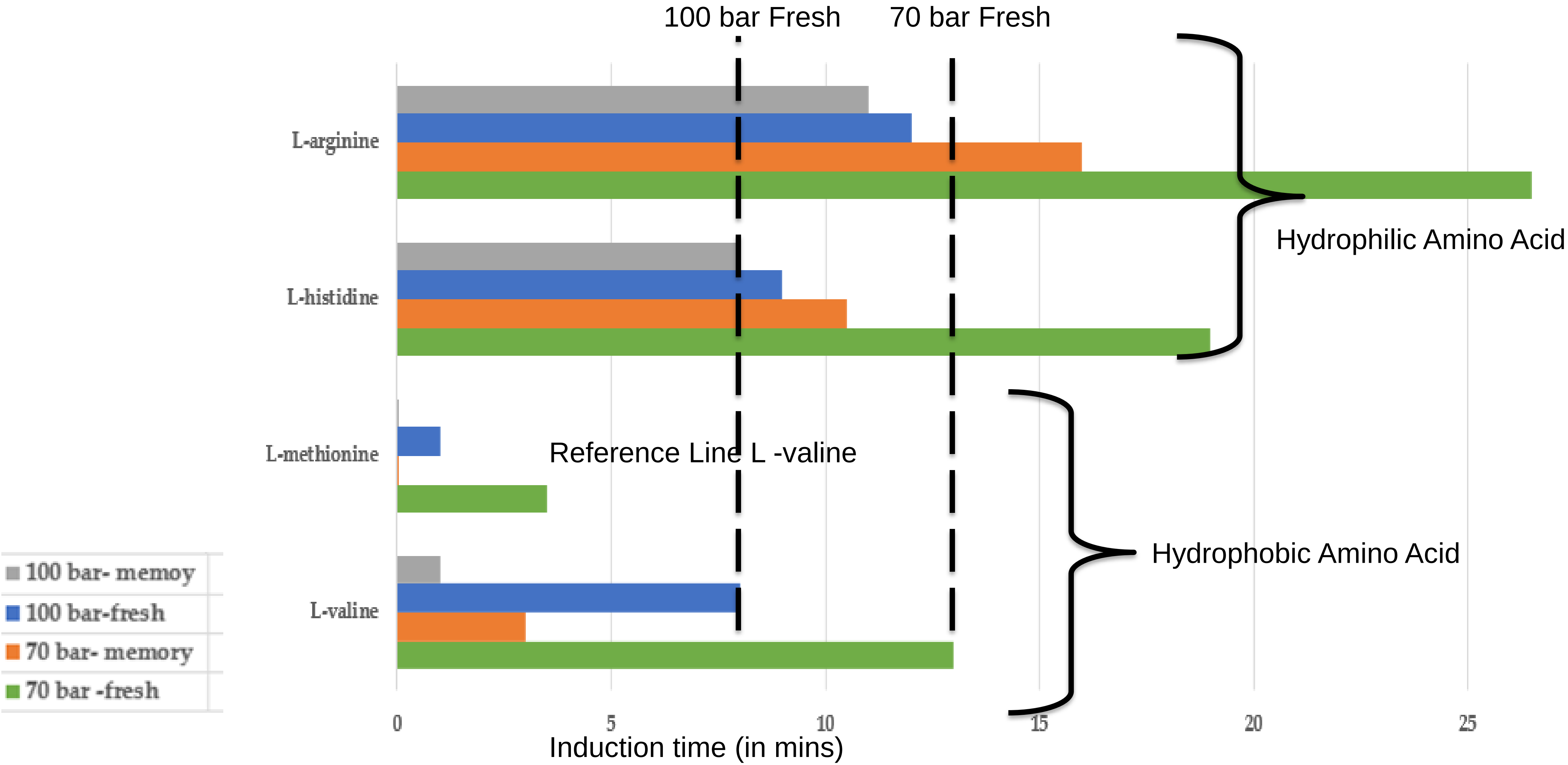
P-T Curve at Constant Volume in Batch system



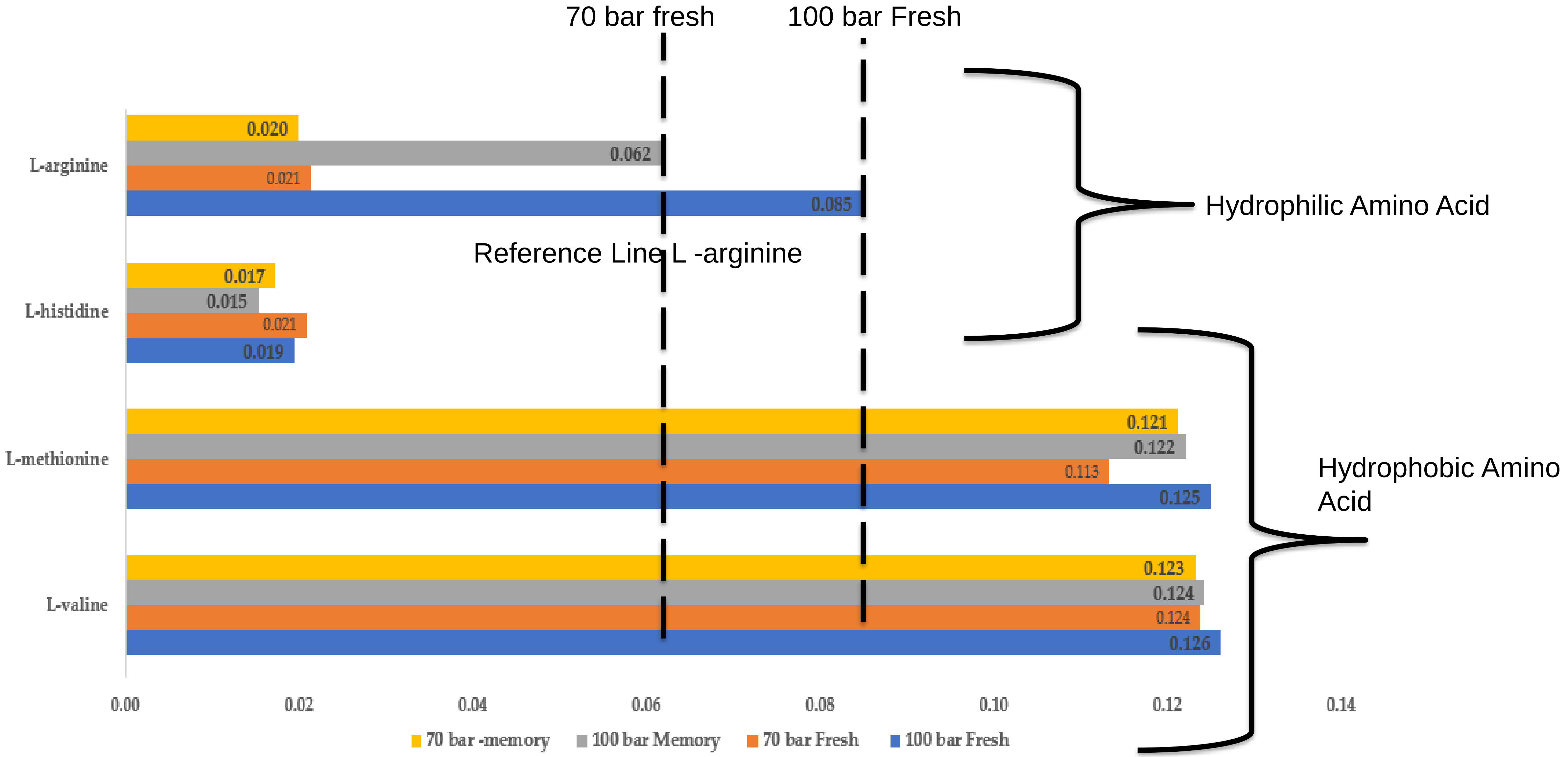
Gas consumption (Gas uptake) curve



Induction time (in mins) for given Amino acids at 1 º C



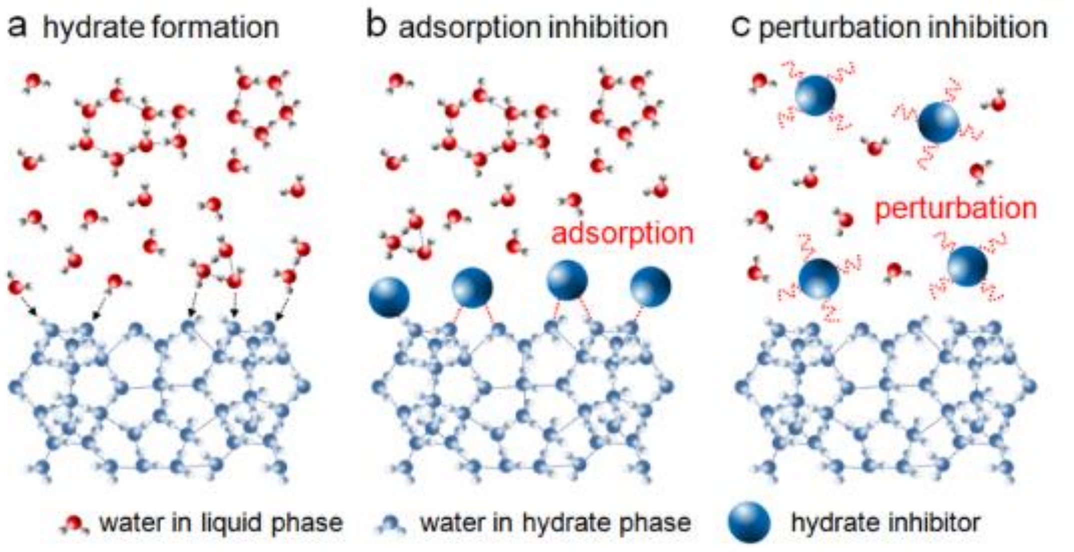
Normalized Gas Uptake (m-mol/m-mmol) for given Amino acids at 1 º C

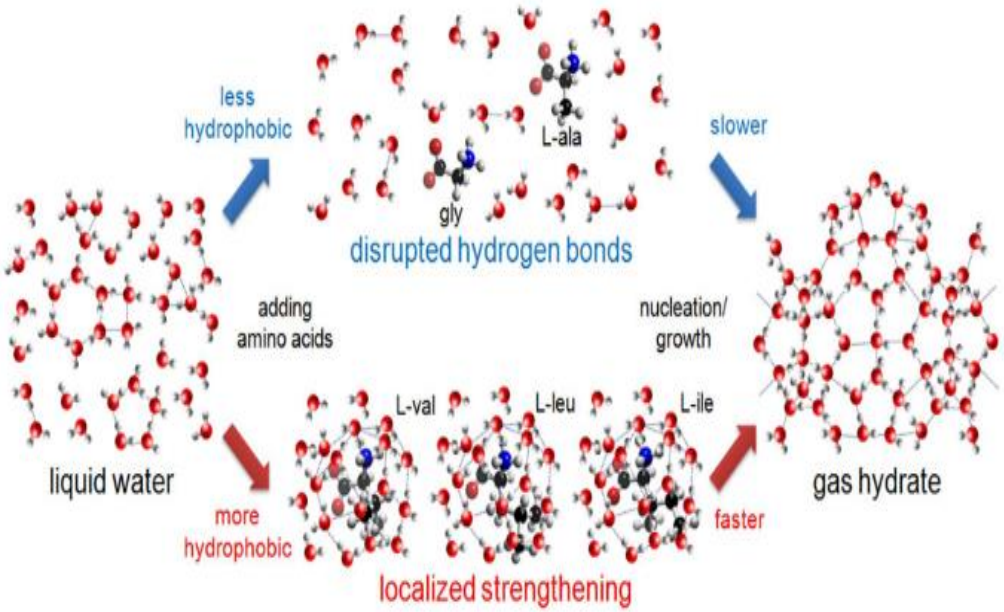


Summary

- Hydrophobic amino acids, as promoter while hydrophilic amino acid as inhibitor
- Hydrophobic amino acids in gas hydrate promotion such as gas storage, capture etc
- Hydrophilic amino acids in flow assurance in Oil & Gas pipeline
- Amino acid shows memory effect in Induction time, kills memory effect in gas uptake.
- Increase in pressure create higher driving force, thus lower induction time and higher gas uptake
- L-methionine is best promoter while L histidine is best inhibitor.

Mechanism





Water molecules in liquid phase are connected through a hydrogen bond network (a) In the system without inhibitor, liquid water molecules close to the hydrate surfaces (e.g. nuclei and bulk surfaces) or solid substrates (e.g. reactor walls, foreign impurities) participate in hydrate formation. (b) The adsorption inhibition hypothesis involves adsorption of the inhibitors on the hydrate surface or any nucleating sites, inhibiting hydrate formation. (c) The perturbation inhibition hypothesis involves perturbation of the organization of local water molecules, preventing hydrate formation.

Less hydrophobic amino acids disrupt hydrogen bonds between water molecules to inhibit hydrate formation while more hydrophobic amino acids strengthen the local organization of the water structure.

that

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