MOLECULAR DYNAMICS ANALYSIS OF PALMITIC ACID IN DEEP EUTECTIC SOLVENTS OF BETAINE AND GLYCEROL

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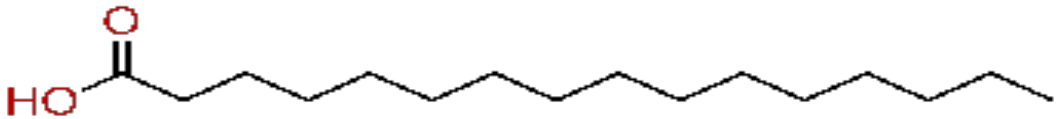
Introduction

- Free fatty acid is fatty acid which is obtained from fat hydrolisis.
- Free fatty acid is one of quality indicator from crude palm oil.
- Crude palm oil according to SNI 01-2901-2006 not allowed to contain more than 5% free fatty acid
- Palmitic acid is free fatty acid that is dominant in crude palm oil (cooking oil).

Palmitic Acid

- Palmitic acid ($CH_3(CH_2)_{14}COOH$) also called Hexadecanoic acid
- Solid form at room temperature, melt at 63,1^{o} C.



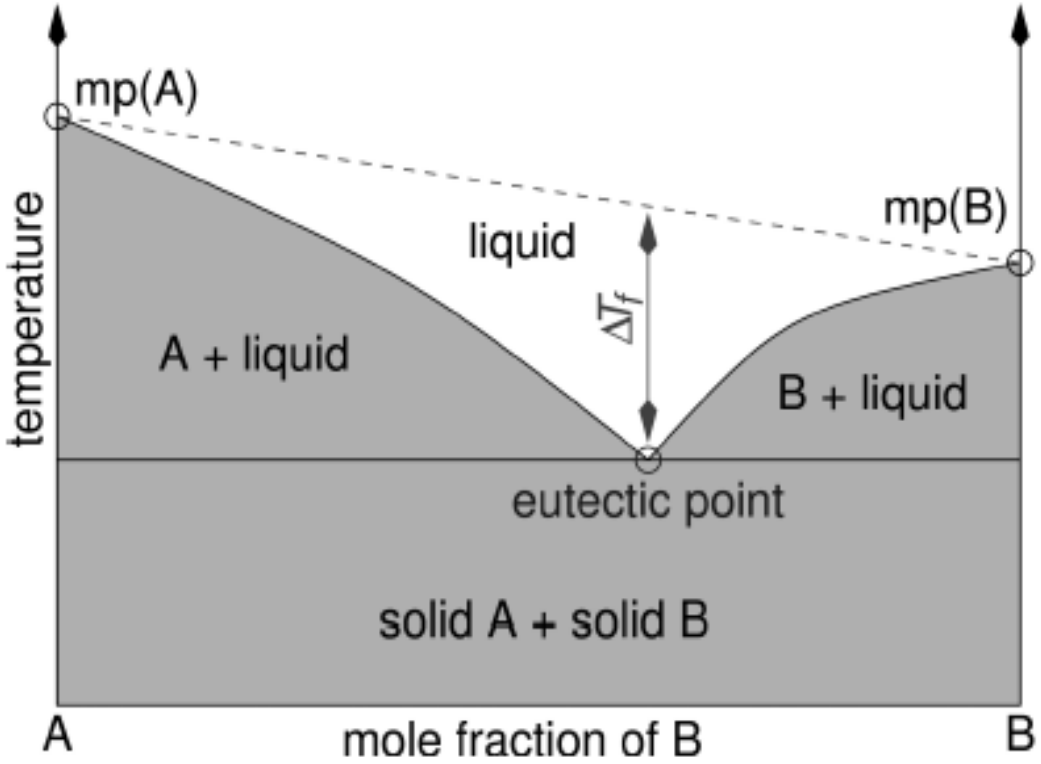
Introduction(2)

- Green chemistry technology currently is an important topic on chemistry study.
- One of green chemistry technology that is currently studied is trying to replace current harsh organic solvent with ionic liquid solvents.

Introduction(3)

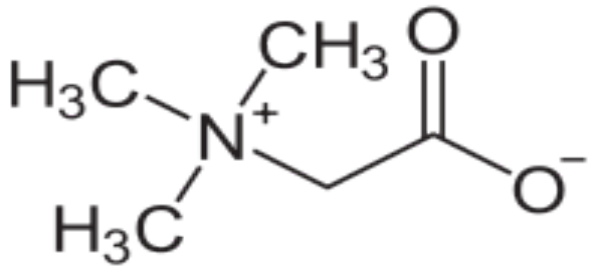
- Deep Eutectic Solvents(DES) is a mixture of ionic liquid solvents which forms is liquid at room temperature. (Abbott et al., 2003)
- The solvent's compound, usually, have a solid form at room temperature.
- After the compounds mixed they will be in liquid form and will be stable for a long time.
- It's mainly because of the formation of hydrogen bond between the molecule. (Abbott et al., 2004)
- Deep eutectic solvents which used organic compounds as the ingredients is called Natural Deep Eutectic Solvents/NADES.

Eutectic Solvents Phase Diagram



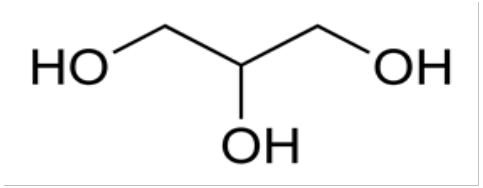
Betaine

- Betaine, also called Betaine anhydrate or Trimethylglycine (TMG).
- Is a metabolyte which obtained naturally.
- On Ionic Liquid, Betaine works as ammonium quartener salt.



Glycerol

- Glycerol is organic compound that is liquid, without smell and color.
- This compound is stable and has a high boiling point.
- On ionic liquid, glycerol works as hydrogen bond donor (HBD)



Introduction(4)

- Direct experiment in laboratory without in silico study will waste much time, effort, and expense.
- In the effort to shorten the experiment time in laboratory we do method of virtual simulation with the aid of computer (molecular dynamic simulation).

Introduction(5)

- Molecular dynamic is a computer simulation of physical atom or molecule movement (Alder, 1959.)
- Molecular dynamic simulation have been performed since 1960s, but for ionic liquid it was performed in 2001.
- Molecular dynamic simulation can give information about total energy, RDF, density, hydrogen bond, diffusion coefficient, etc.

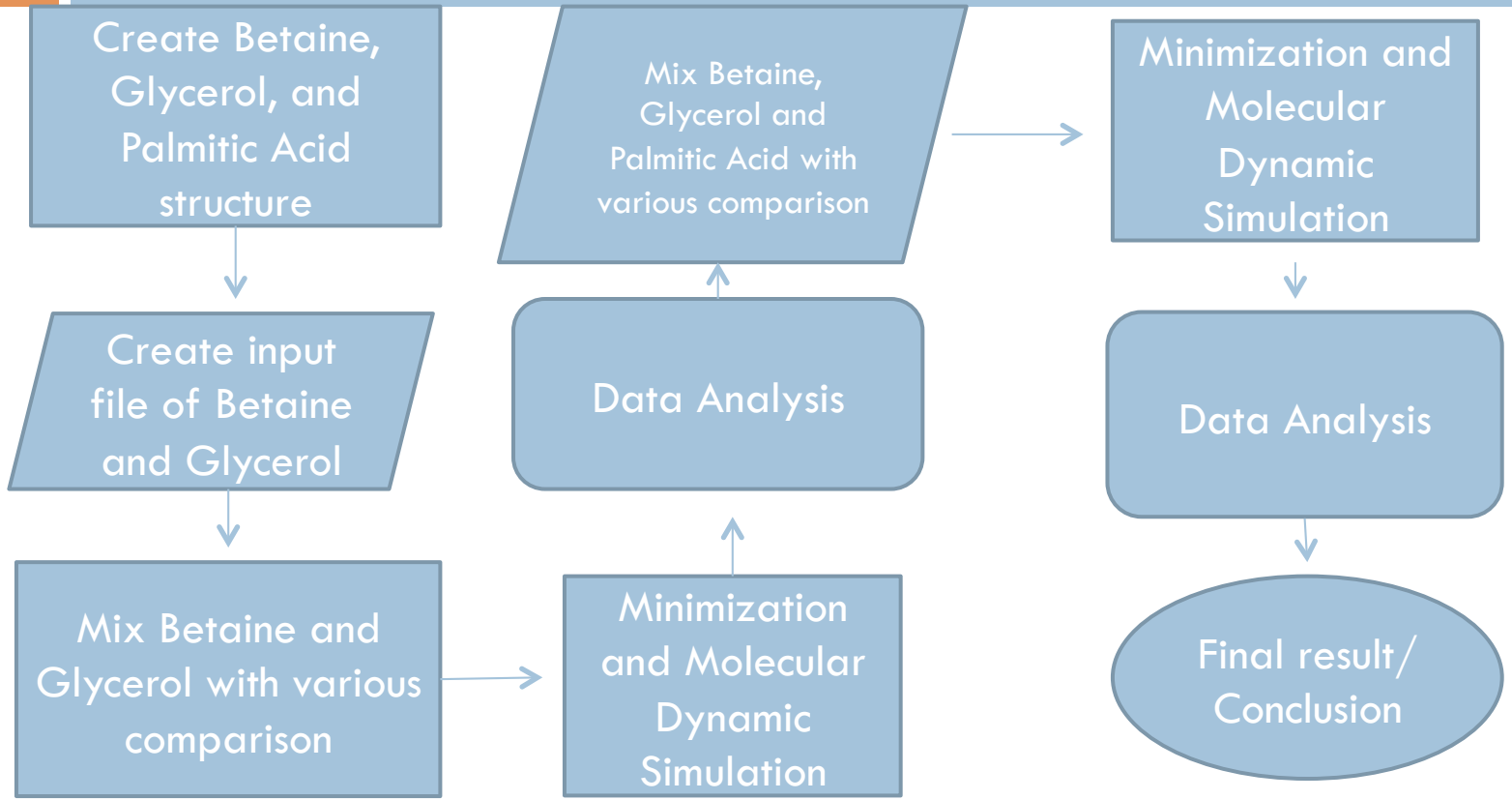
Problem description

- Which composition of Betaine, Glycerol will create most stable mixture?
- Is palmitic acid can interact with the mixed solvent?

Research Goal

- Perform simulation of Betaine and Glycerol as Deep Eutectic Solvent (DES).
- Determine the best composition of Deep Eutectic Solvents (DES)
- Understanding interaction of Palmitic Acid in mixed solvent.

Work Scheme


Create Betaine, Glycerol, and Palmitic Acid structure
Create input file of Betaine and Glycerol
Mix Betaine and Glycerol with various comparison
Minimization and Molecular Dynamic Simulation
Data Analysis
Mix Betaine, Glycerol and Palmitic Acid with various comparison
Minimization and Molecular Dynamic Simulation
Data Analysis
Final result/ Conclusion

Tools

- Hardware: A set of computer with specification: RAM 32 GB, Intel dual eight core Xeon E5620 Processor, **GPU NVIDIA GeForce GTX 780**. NBCR Cluster.
- Software: Linux 12.04 LTS, GaussView and Gaussian09W, Packmol, OpenBabel, AmberTools 13, **Amber 11**, UCSF Chimera, MarvinSketch, Avogadro, PuTTY, dan VMD.

Source

- 3D structure of Palmitic Acid
- 3D structure of NADES solvent (Betaine and Glycerol)

Working Methods

- Preparation
- Molecular Dynamic Simulation
- Analysis

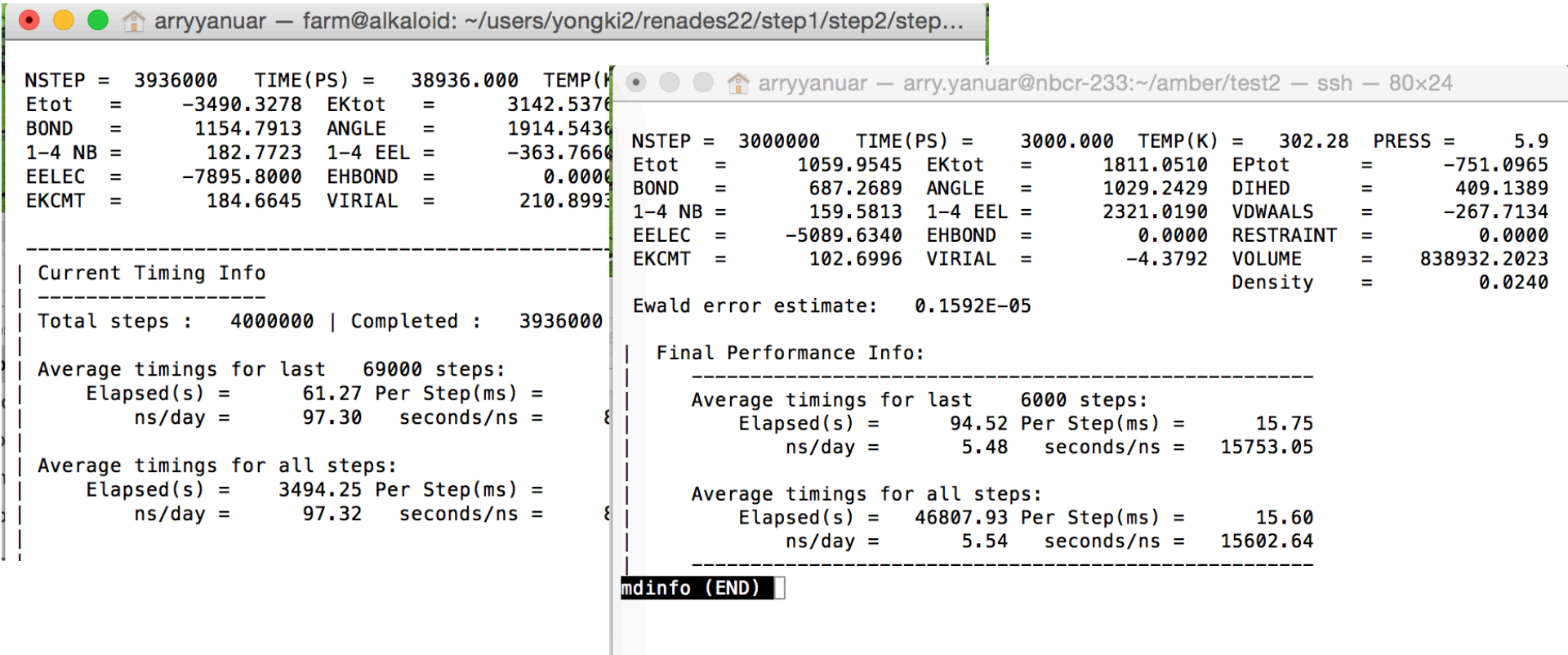
Molecule Composition

	Composition					
Compound	**1:1**	**1:1 + Palmitic Acid**	**1:2**	**1:2 + Palmitic Acid**	**2:3**	**2:3 + Palmitic Acid**
Betaine	100	100	50	50	100	100
Glycerol	100	100	100	100	150	150
Palmitic Acid	-	10	-	20	-	20

Comparison of Simulation Time with CPU and GPU

Simulaton process	Average of simulation time (ns/day)	CPU time (s) or (hr)
Processor (Intel Xeon E5620) 1 Processor	0,94	276016,46 (76.67)
GPU (Nvidia GeForce GTX780)	84,45	4092,38 (1.14)

GPU and NBCR Cluster (approx timing)

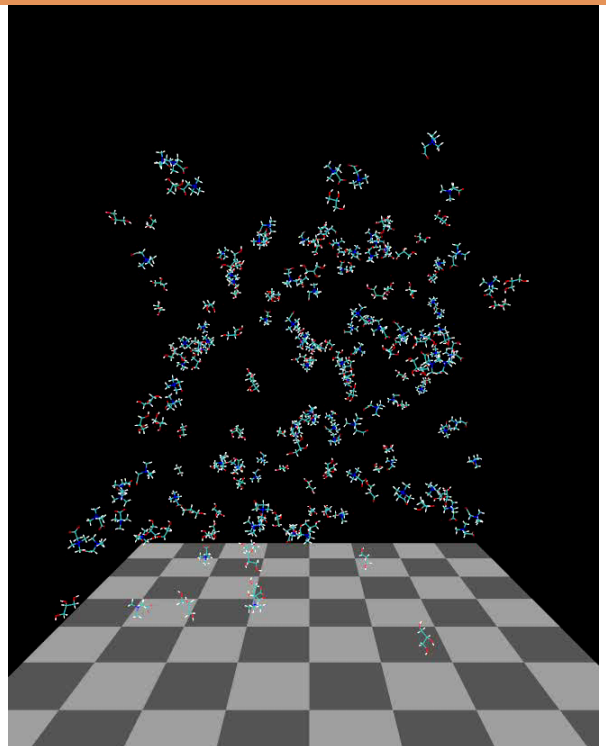


Data Analysis

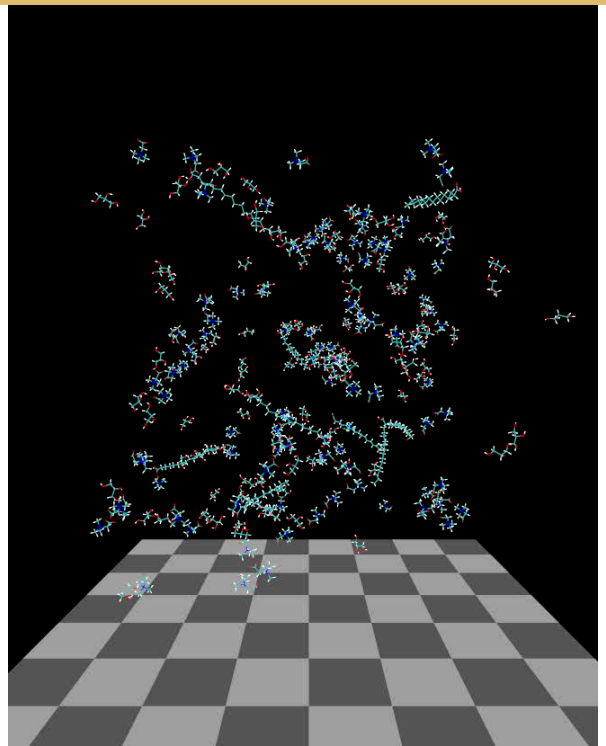
1. Analyze Density and Total Energy
2. After the system stabilized then perform analysis of RDF and hydrogen bond

Visual Appearance (Demo)

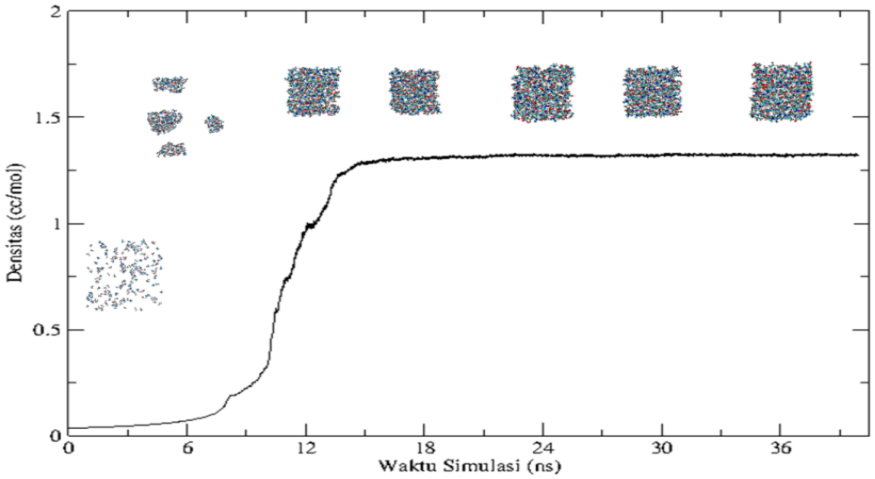
Composition 1:1



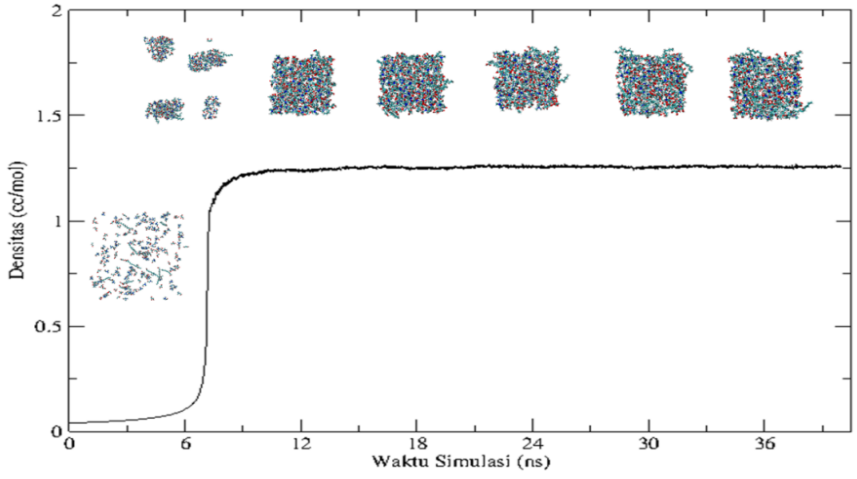
Composition 1:1 + Palmitic Acid



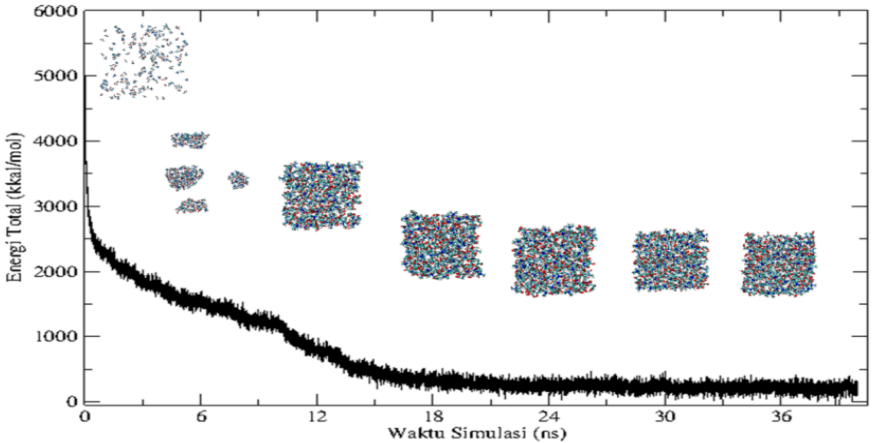
Densitas Betain:Gliserol (1:1)



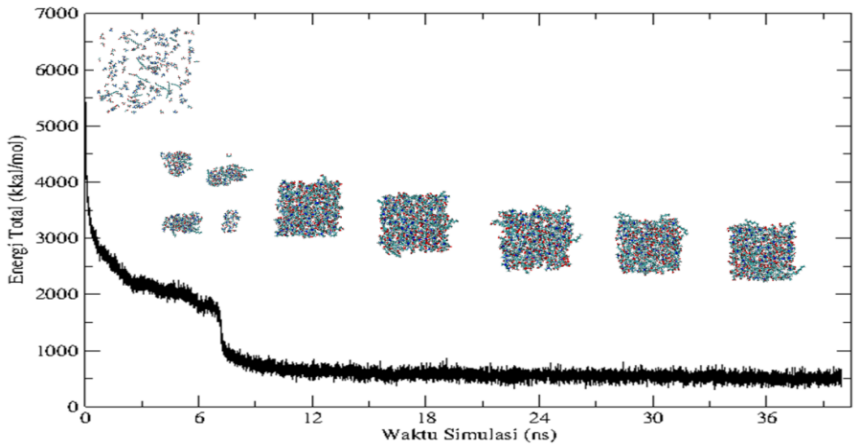
Densitas Betain:Gliserol (1:1) + Asam Palmitat



Energi Total Betain:Gliserol (1:1)

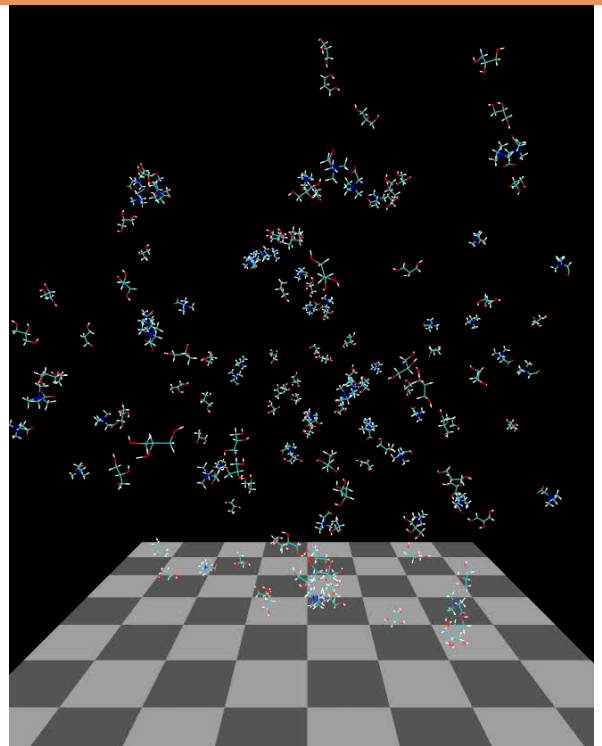


Energi Total Betain:Gliserol (1:1) + Asam Palmitat

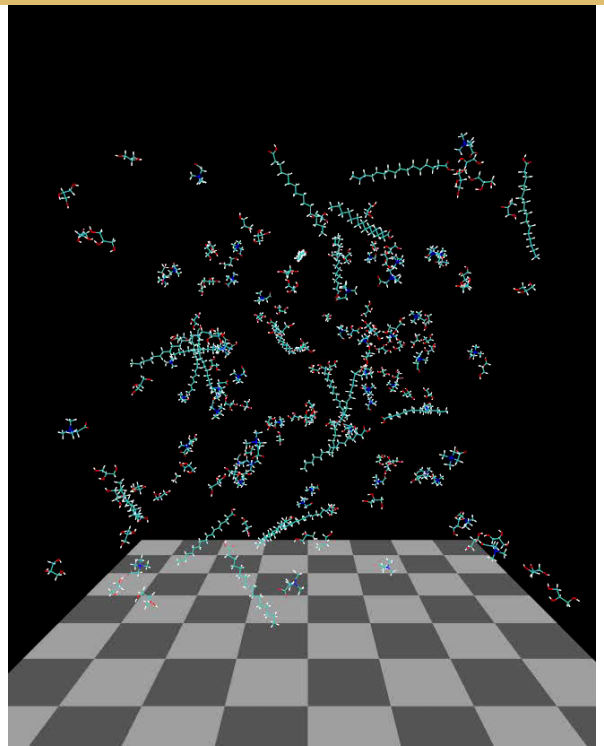


Visual Appearance (Demo)

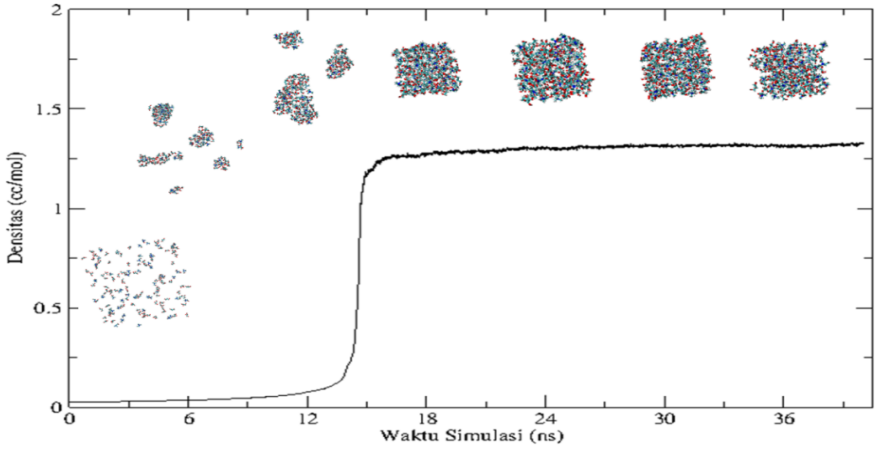
Composition 1:2



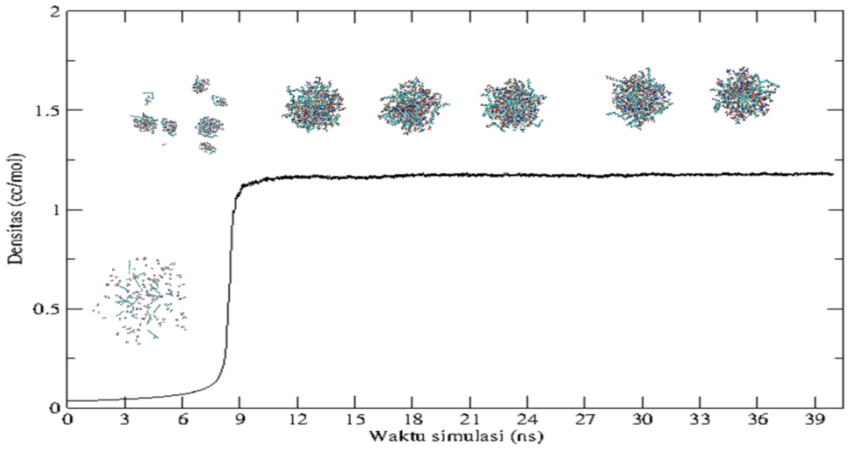
Composition 1:2 + Palmitic Acid



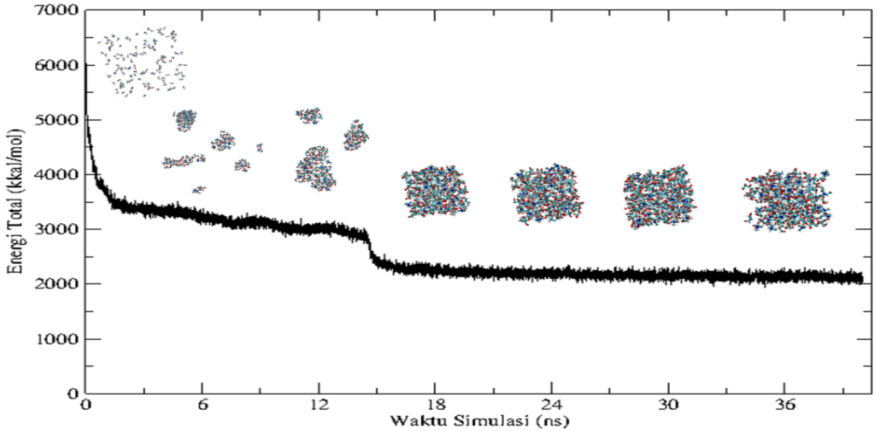
Densitas Betain:Gliserol (1:2)



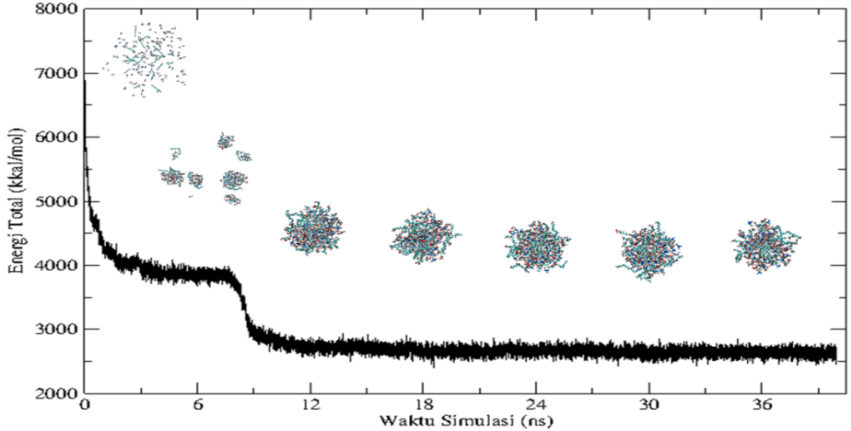
Densitas Betain:Gliserol (1:2) + Asam Palmitat



Energi Total Betain:Gliserol (1:2)

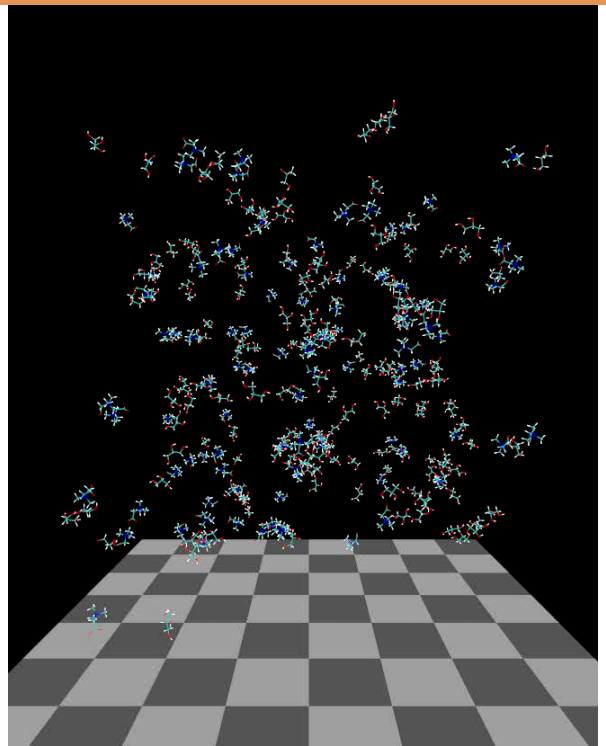


Energi Total Betain:Gliserol (1:2) + Asam Palmitat

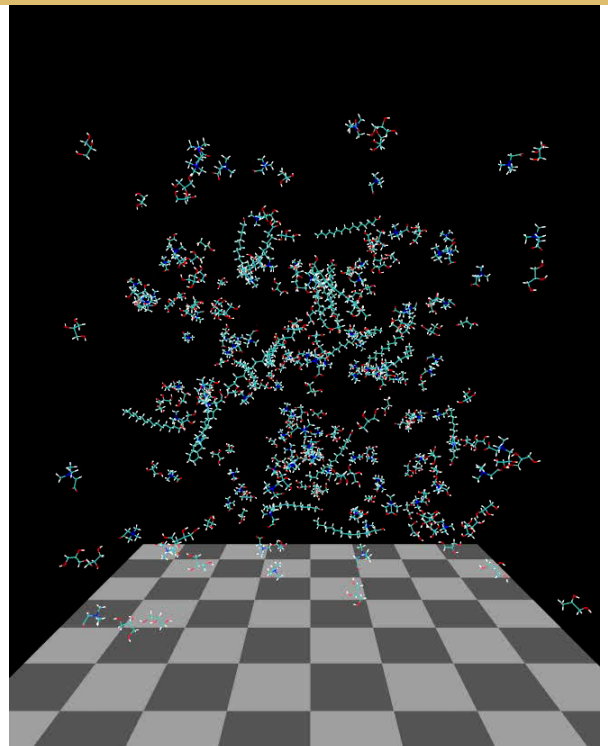


Visual Appearance (Demo)

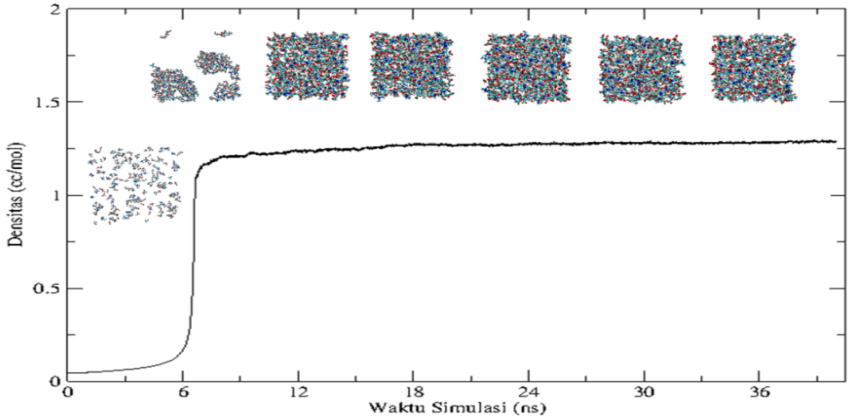
Composition 2:3



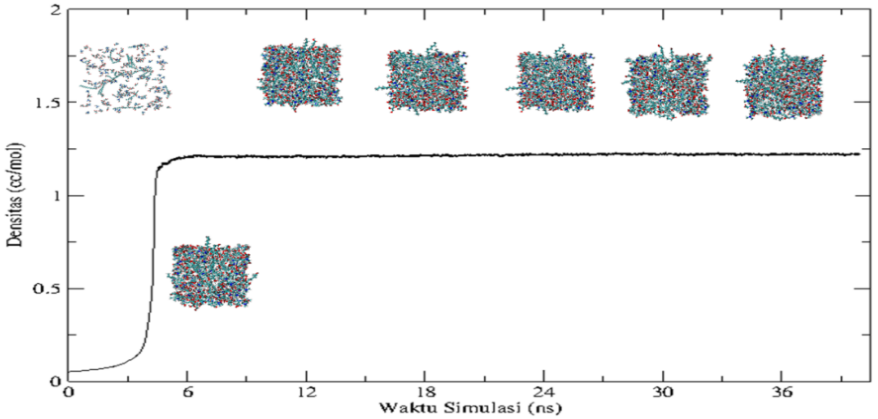
Composition 2:3 + Palmitic Acid



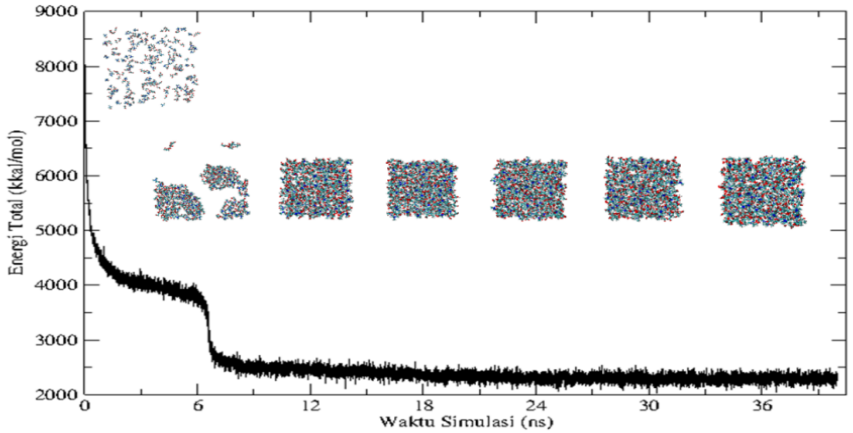
Densitas Betain:Gliserol (2:3)



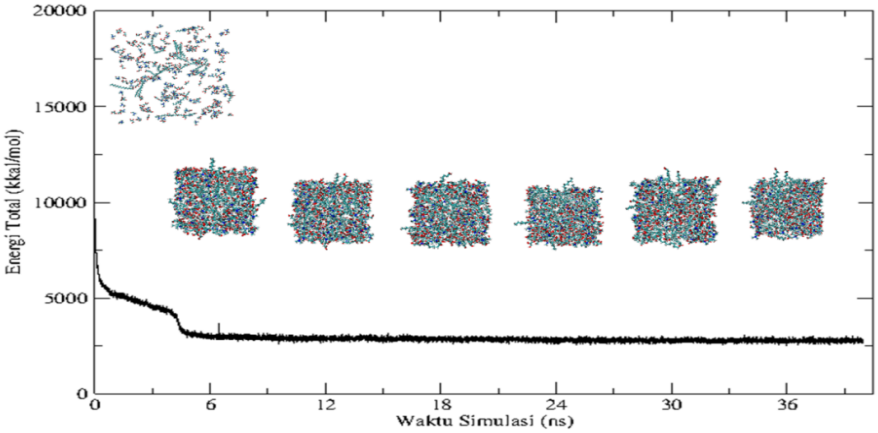
Densitas Betain:Gliserol (2:3) + Asam Palmitat



Energi Total Betain:Gliserol (2:3)



Energi Total Betain:Gliserol (2:3) + Asam Palmitat

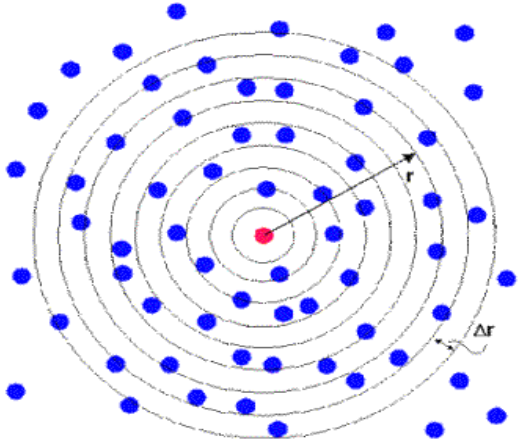


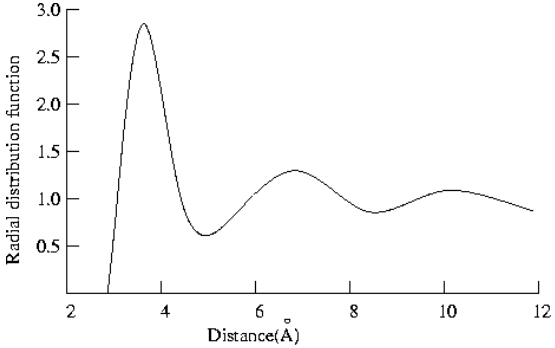
Density Table & Total Energy Analysis

Composition (Betain : Glycerol)	Average Density(cc/mol)	Average Total Energy (kkal/mol)
1:1	1,32252	203,341
1:1 + Palmitic Acid	1,25608	504,757
1:2	1,3189	2125,29
1:2 + Palmitic Acid	1,17843	2634,13
2:3	1,28559	2293,35
2:3 + Palmitic Acid	1,22091	2778,4

Radial Distribution Function

- Radial Distribution Function (RDF) is a correlation function of a pair, which describe how, average, atoms each other in a radial system. (Côté, Smith & Lindan, 2001).
- Mathematically defined as $g(r)=n(r)/(\rho\, 4\pi\, r^2\, \Delta r)$

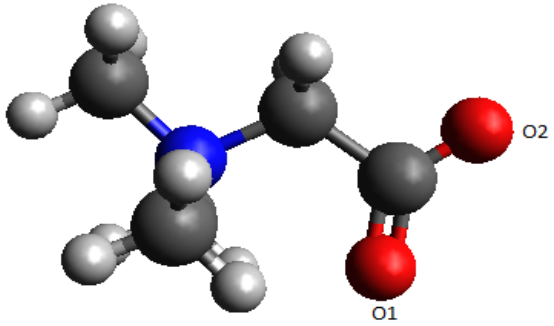


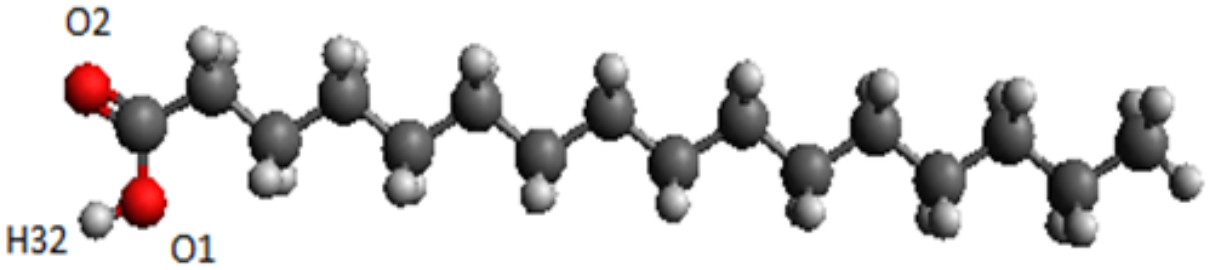


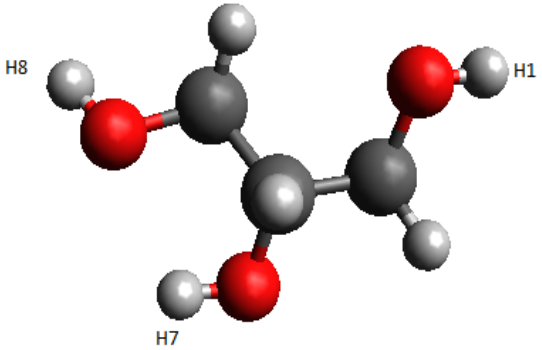
Radial Distribution Function (2)

- Radial Distribution Function obtained from trajectory when the graphic is already stabilised.
- Radial Distribution Function can be used as one of indicator for bond between atoms.
- This is because RDF counts the probability of an atom to find another atom in certain distance.

The Number of Atom Analyzed

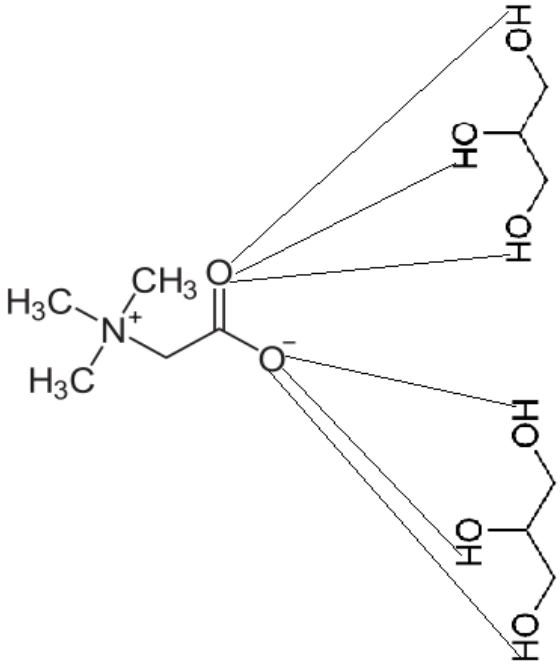


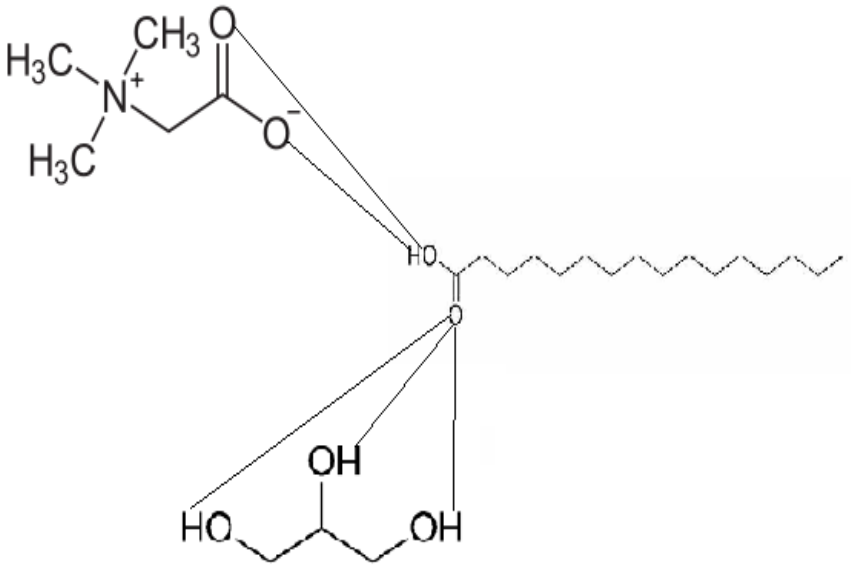




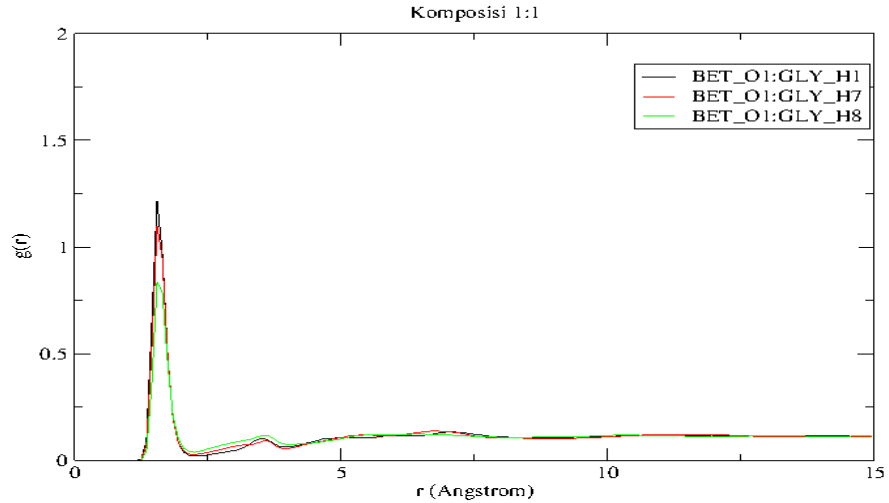
RDF only analyzed at atoms which have potency to bonded, which is O atom on Betaine, H1, H7 and H8 atoms on Glycerol and O2 and H32 atoms on Palmitic Acid

RDF and Hydrogen Bond Analysis (hypothesis)

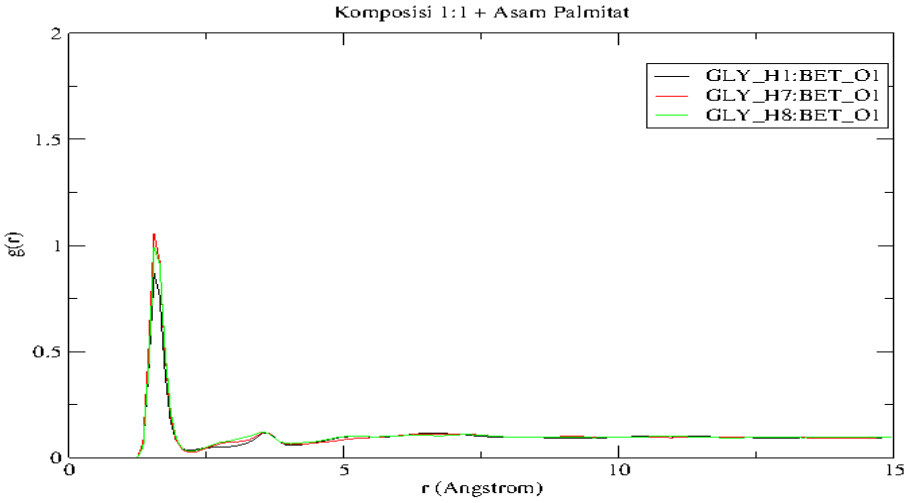




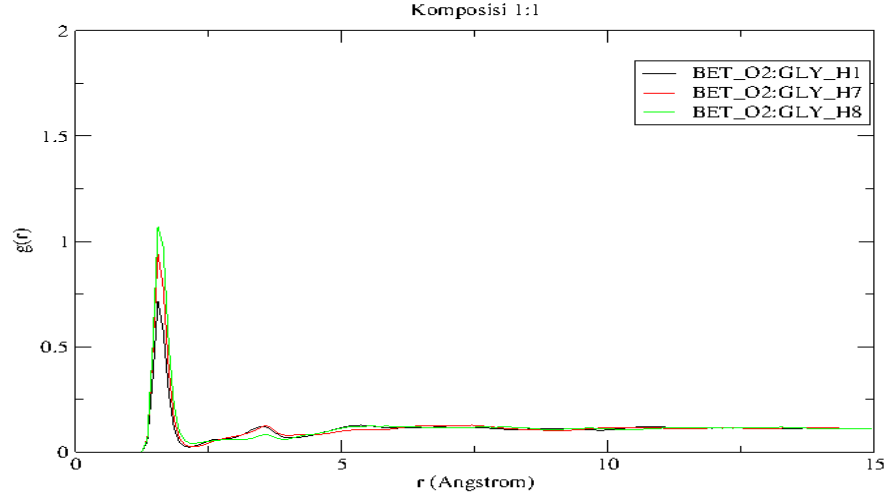
Fungsi Distribusi Radial Atom O1 Betain terhadap Atom H Gliserol



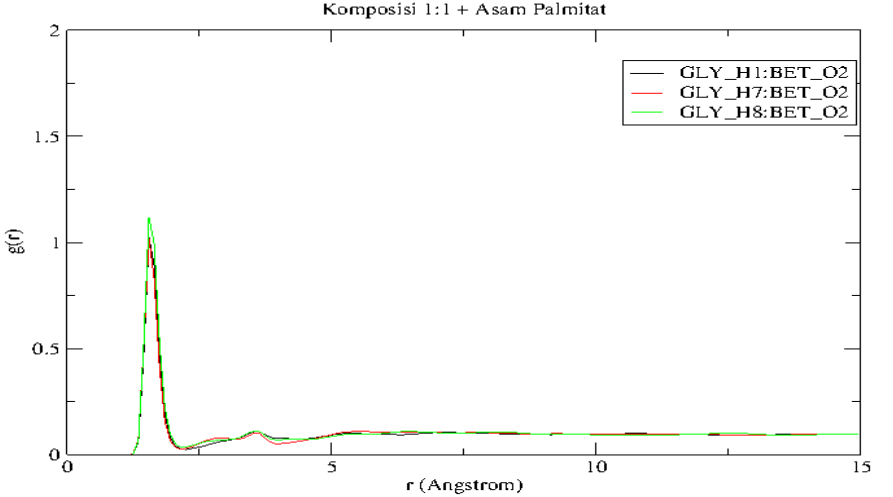
Fungsi Distribusi Radial Atom H Gliserol terhadap Atom O1 Betain



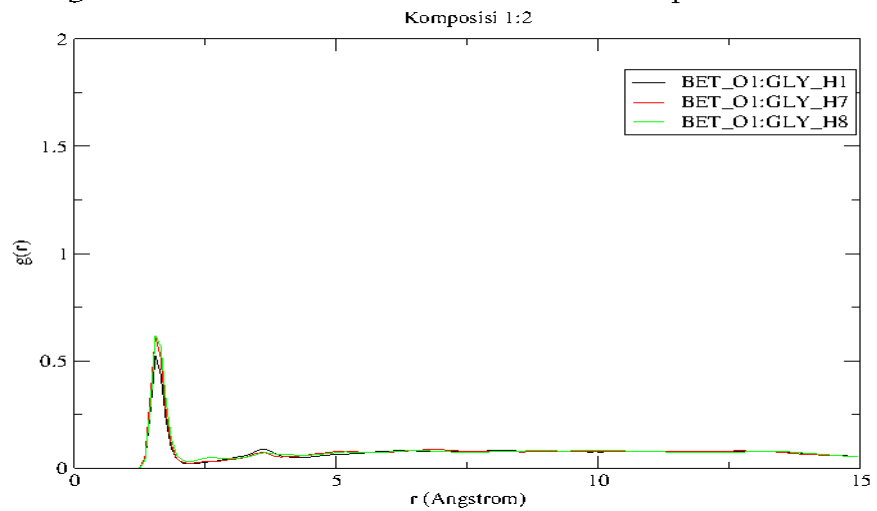
Fungsi Distribusi Radial Atom O2 Betain terhadap Atom H Gliserol



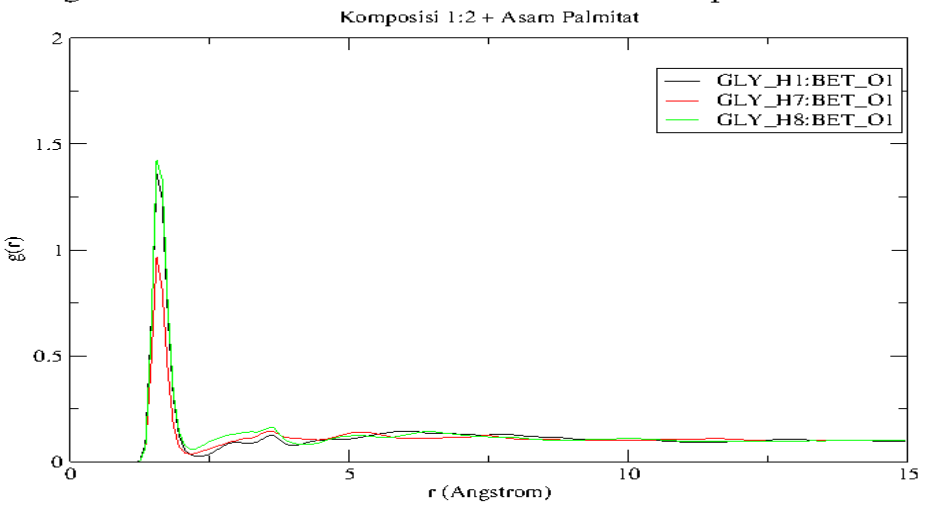
Fungsi Distribusi Radial Atom H Gliserol terhadap Atom O2 Betain



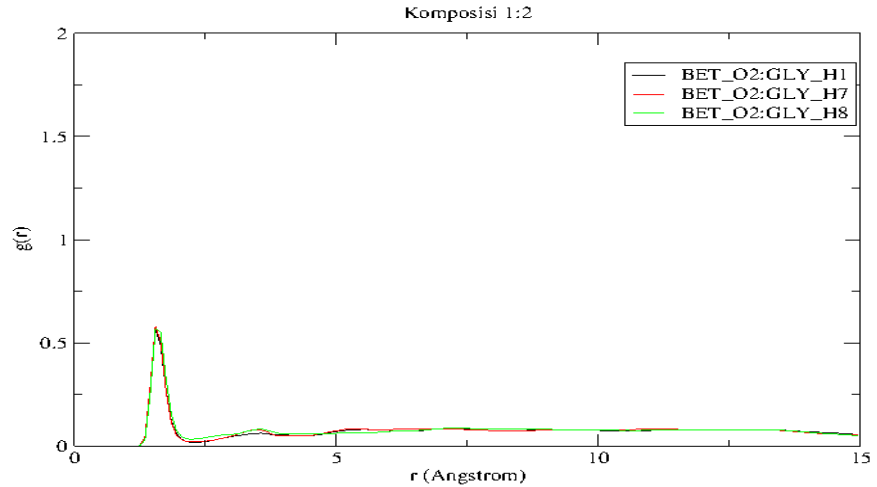
Fungsi Distribusi Radial Atom O1 Betain terhadap Atom H Gliserol



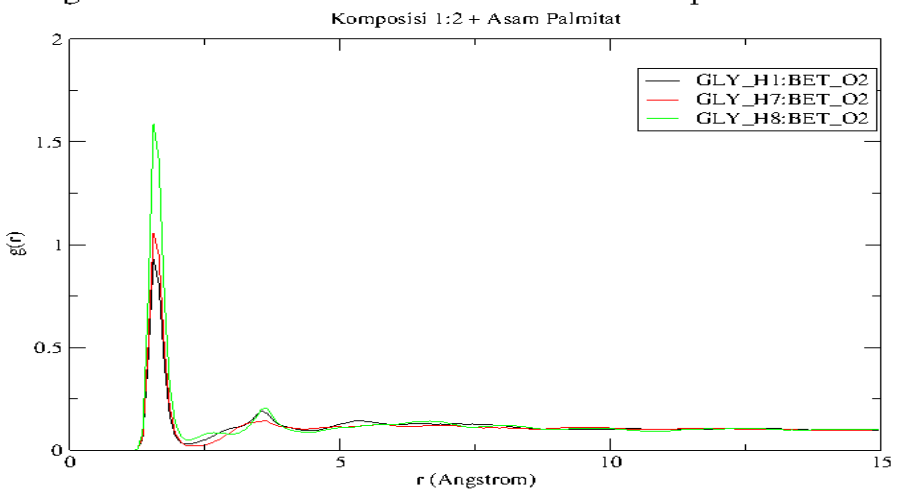
Fungsi Distribusi Radial Atom H Gliserol terhadap Atom O1 Betain



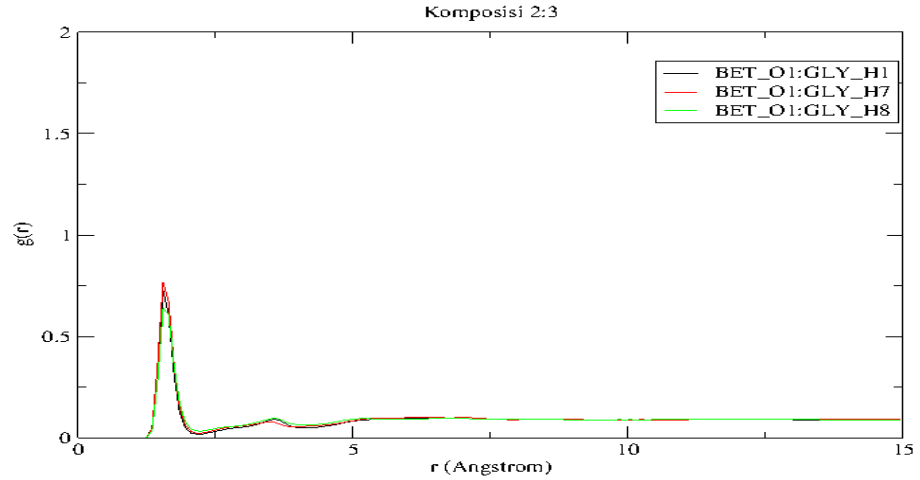
Fungsi Distribusi Radial Atom O2 Betain terhadap Atom H Gliserol



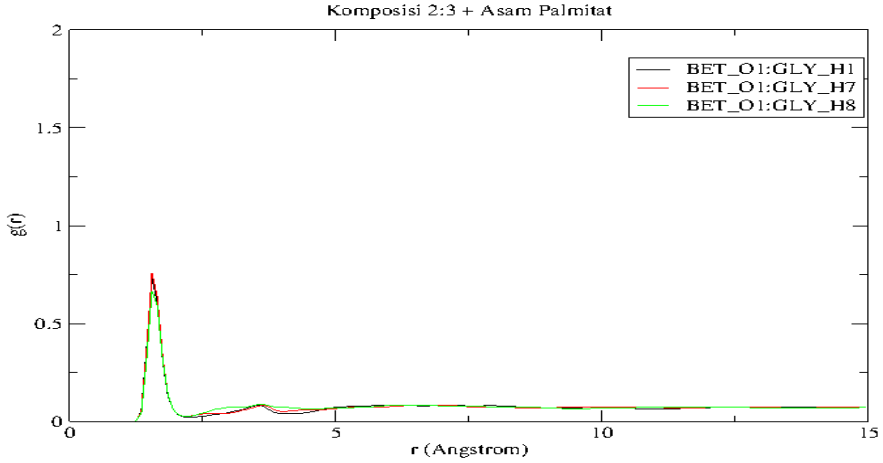
Fungsi Distribusi Radial Atom H Gliserol terhadap Atom O2 Betain



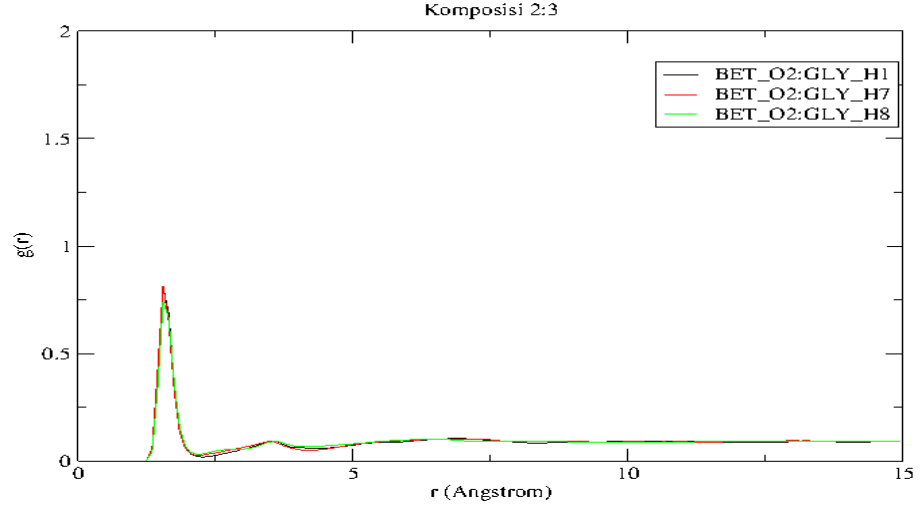
Fungsi Distribusi Radial Atom O1 Betain terhadap Atom H Gliserol



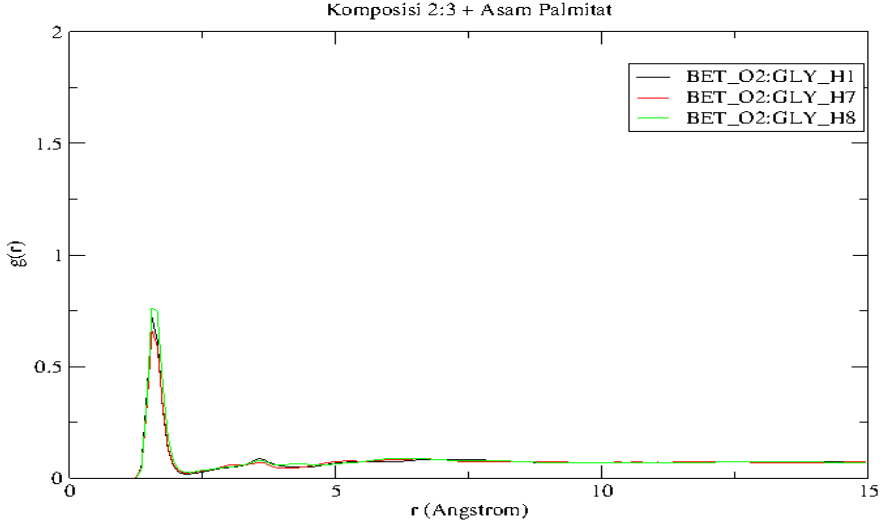
Fungsi Distribusi Radial Atom O1 Betain terhadap Atom H Gliserol



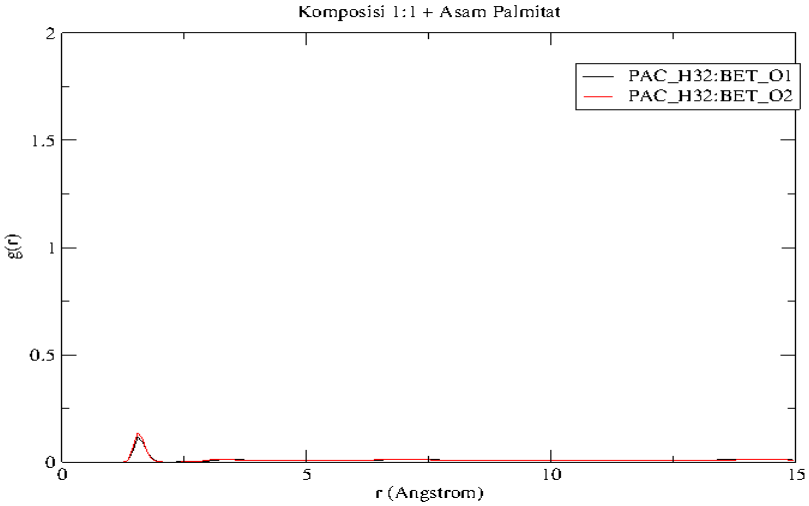
Fungsi Distribusi Radial Atom O2 Betain terhadap Atom H Gliserol



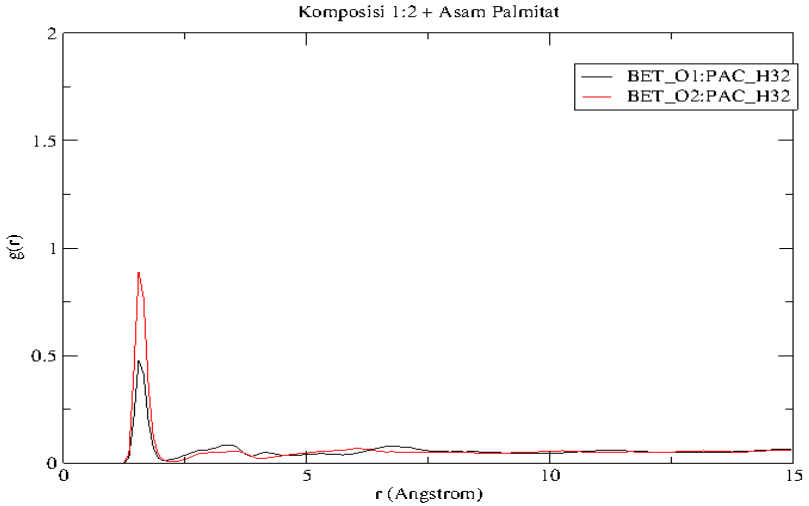
Fungsi Distribusi Radial Atom O2 Betain terhadap Atom H Gliserol



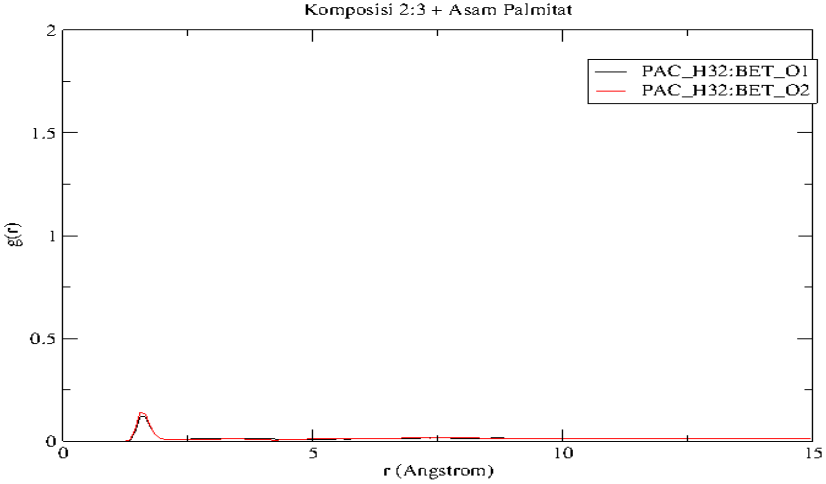
Fungsi Distribusi Radial Atom H32 Asam Palmitat terhadap Atom O Betain



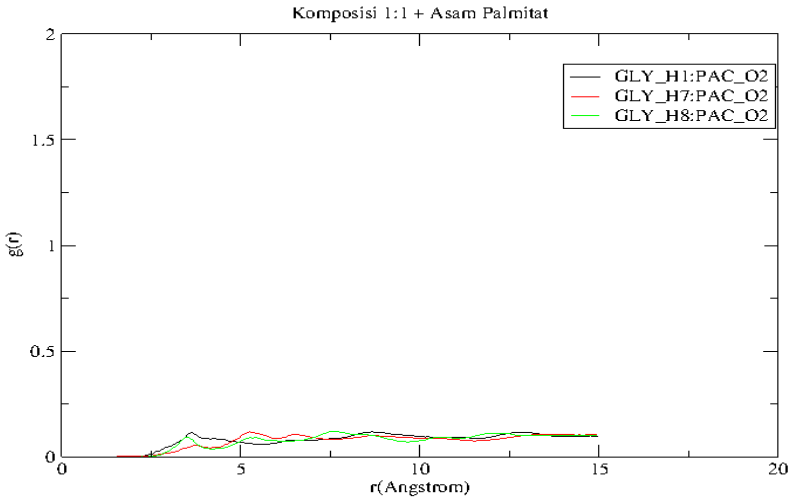
Fungsi Distribusi Radial Atom O Betain terhadap Atom H32 Asam Palmitat



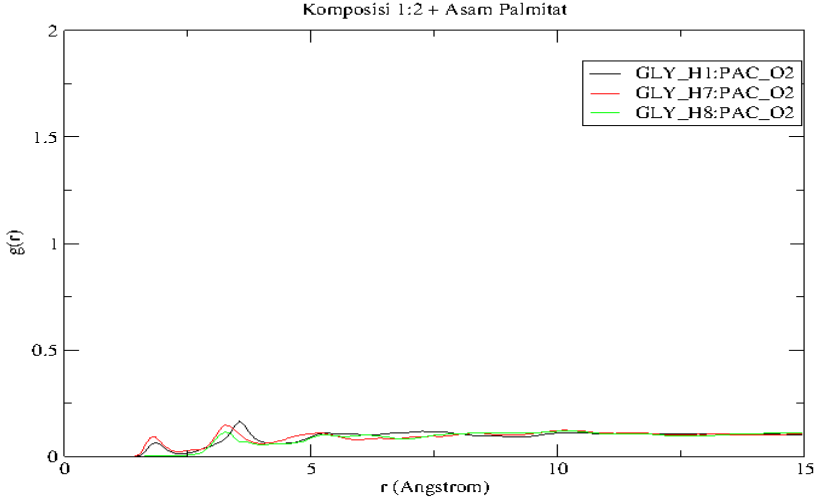
Fungsi Distribusi Radial Atom H32 PAC terhadap Atom O Betain



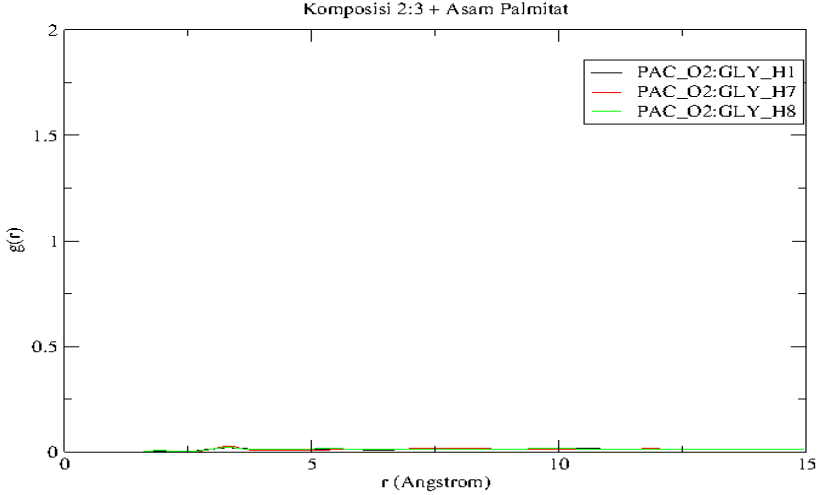
Fungsi Distribusi Radial Atom H Gliserol terhadap Atom O2 Asam Palmitat



Fungsi Distribusi Radial Atom H Gliserol terhadap Atom O2 Asam Palmitat



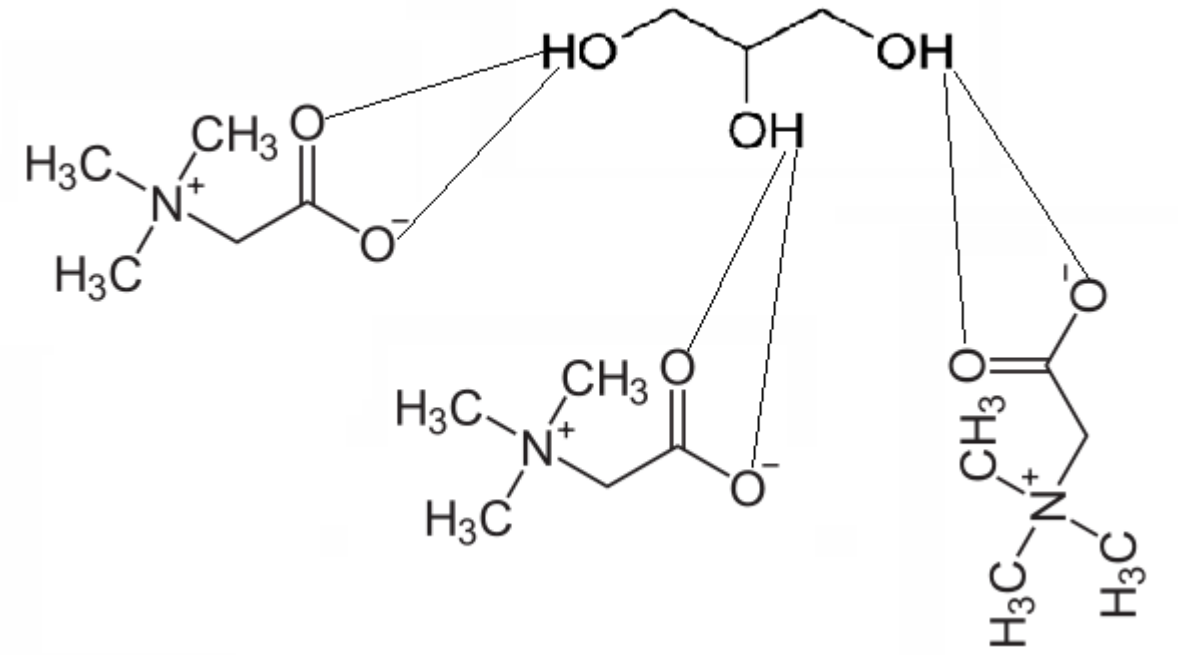
Fungsi Distribusi Radial Atom O2 Asam Palmitat terhadap Atom H Gliserol



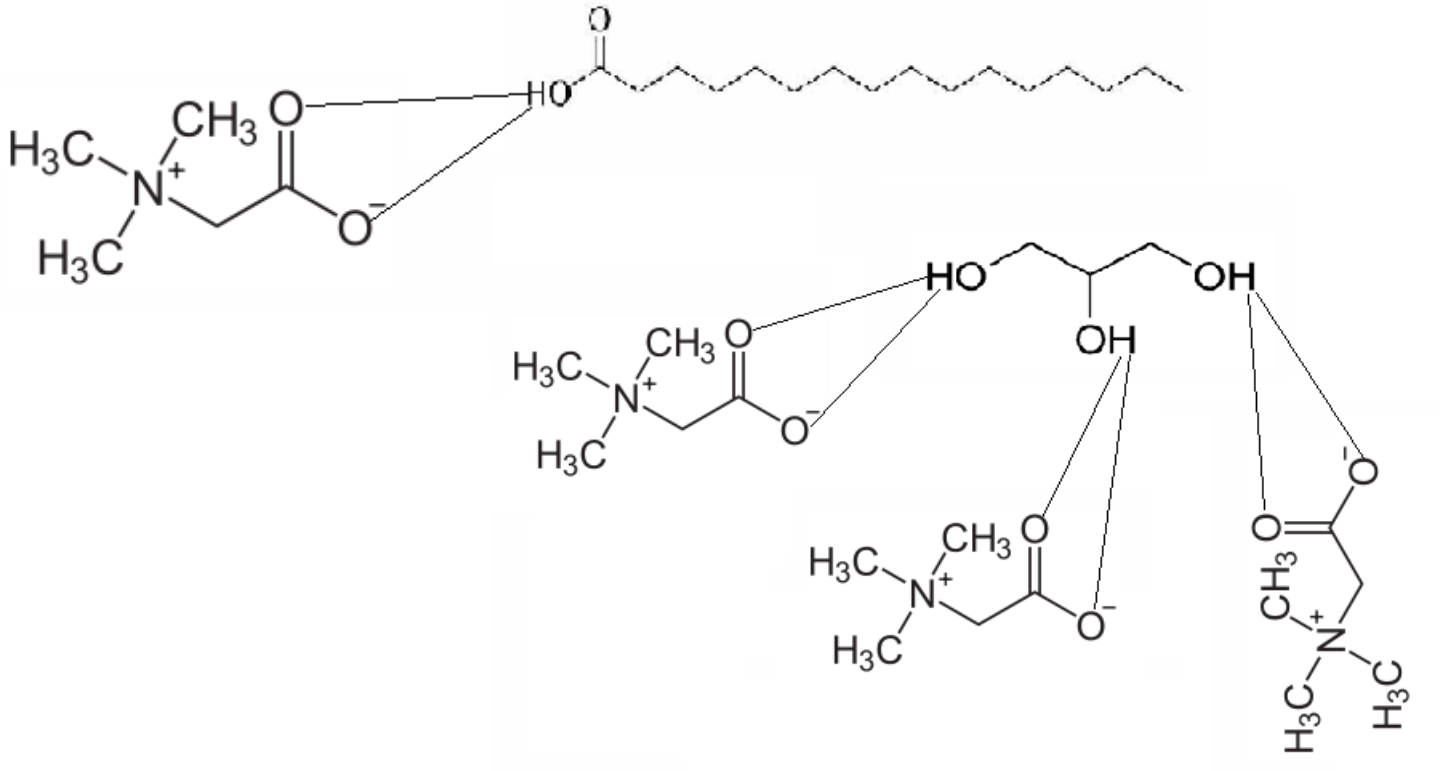
Hydrogen Bond Table

	H7 with O Betaine		H1 with O Betaine		H8 with O Betaine		H32 Palmitic Acid with O Betain	
Composition	Amount of Bond	Maximum Occupancy (%)	Amount of Bond	Maximum Occupancy (%)	Amount of Bond	Maximum Occupancy (%)	Amount of Bond	Maximum Occupancy (%)
1:1	55	56,44	40	52,42	67	51,67	-	-
1:1 + Palmitic Acid	74	41,35	78	41,84	92	39,20	6	17,38
1:2	46	39,65	61	35,95	61	33,24	-	-
1:2 + Palmitic Acid	37	29,94	36	49,46	45	40,63	6	25,89
2:3	70	56,59	84	50,86	87	49,44	-	-
2:3 + Palmitic Acid	59	43,04	67	51,07	82	49,86	7	13,32

Hydrogen Bonds between Betaine and Glycerol (simulation result)



Hydrogen Bonds between Glycerol, Betaine and Palmitic Acid (simulation result)



Conclusion

- The best mixture obtained are 1:2 dan 2:3
- Palmitic Acid can make hydrogen bonds with the solvent mixture between Betaine and Glycerol.
- Hydrogen Bond is formed also in mixture of Betaine and Glycerol and with Palmitic Acid.
- Palmitic Acid increase mixing process of Betaine and Glycerol.

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THANK YOU