



The Function of Emollients in Skin Care

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Emollient - definition

Wikipedia: “complex mixtures of chemical agents specially designed to make the external layers of the skin (epidermis) softer and more pliable”

‘Emollire’ (Latin) – means to soften

Emollients are usually:

- the main component in emulsions after water (3-20% or more) dominating ingredient in many anhydrous formulations
- various chemical structures including vegetable and mineral oils, esters and silicones
- can have different polarities (hydrophilic – lipophilic)
- can have several features at the same time

Despite a definition often found in dictionaries, an emollient is not always equal to a moisturizer

Functions of emollients in cosmetic formulations

- ◆ Skin softening (emolliency)
- ◆ Occlusive moisturization (TEWL)
- ◆ Lubrication
- ◆ Structure formation in formulation
 - ◆ Emulsion, viscosity, hardness, setup
- ◆ Delivery system/solubilizer/carrier
 - ◆ Actives, pigments
- ◆ Aesthetics and sensory modifier



Emollient properties can be measured objectively

- ◆ **Rheology** (Viscosity and/or viscoelasticity)
 - ◆ Consistency - solid fat content, melting profiles
- ◆ **Surface and interfacial properties**
 - ◆ Spreadability (on different substrates, especially skin or hair)
 - ◆ Polarity estimation or measurement
- ◆ Refractive index
- ◆ Stability at different conditions (oxidation, hydrolysis)
- ◆ Solubilization capacity
- ◆ **Interaction with other ingredient groups**



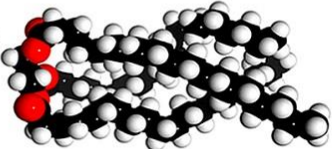


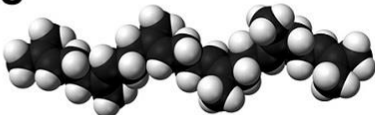
Emollients and skin

- The surface of the skin is a complex system comprising lipids, cells, proteins, microorganisms, water, natural moisturizing factors, etc
- Skin surface lipids are of two types
 - Epidermal lipids
 - Sebum lipids
- Epidermal lipids (from keratinocytes)
 - Ceramides, cholesterol, free fatty acids
 - Typically extractable from skin surface: 5-10 $\mu\text{g}/\text{cm}^2$
- Sebum lipids (from sebaceous glands)
 - Triglycerides, wax monoesters, squalene, free fatty acids, tocopherols
 - Typically extractable from the forehead: 150-300 $\mu\text{g}/\text{cm}^2$



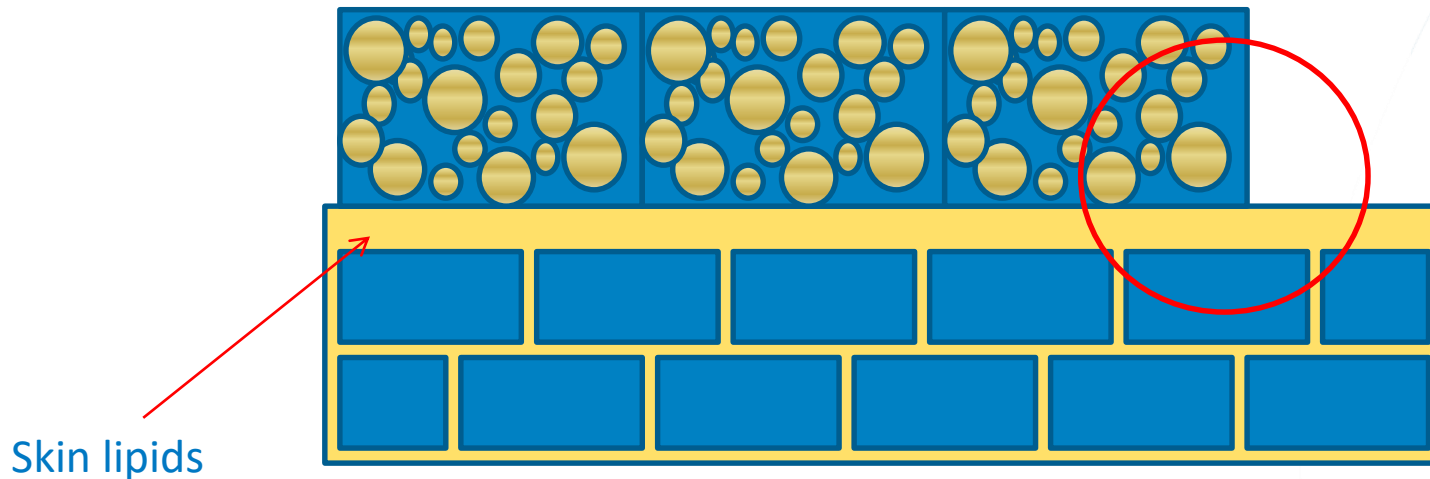
Emollients and skin

Table 1 Components of skin surface lipids

	Sebum %	Epidermal lipids %
Glycerides 	30–50	30–35
Free Fatty Acids 	15–30	8–16
Wax Esters 	26–30	-
Squalenes 	12–20	-
Cholesterol Esters	3.0–6.0	15–20
Cholesterols	1.5–2.5	20–25

Stratum corneum and emollients

- ◆ Sensory properties, moisturization, ingredient absorption and many other properties are determined by the interaction between the stratum corneum and the emollients from the skin care product



Keratinocytes approx 20 micrometer wide
Emulsion droplets 0.1 -5 micrometers in diameter

Physicochemical parameters affecting the interaction

- ◆ **Wetting** of the stratum corneum by the emulsion
 - ◆ Surface & interfacial properties of emulsion droplets versus the properties of the skin lipids
- ◆ **Rheology** of emulsion
 - ◆ Determined by emollient properties and interaction with polymers and emulsifiers
- ◆ **Solubility** of emollient in stratum corneum and vice versa
 - ◆ Polarity of respective phases
- ◆ **Droplet-droplet interaction**
 - ◆ Breaking of emulsion to create an oil film on the SC surface
- ◆ **Skin surface topology**
 - ◆ Smooth versus wrinkled etc



Emollient parameters to consider

- ◆ Polarity determines solubility and solubilisation
- ◆ Polarity is a 3-dimensional property (Hansen model)
 - ◆ Van der Waals interactions (Dispersive forces)
 - Molecular size and shape
 - ◆ Hydrogen bonding
 - Presence of $-OH$, $-COOH$, $-NH_2$ etc groups with mobile hydrogen groups
 - ◆ Polarizability
 - Presence of double bonds, ester and amide groups, aromatic rings etc
 - Measures the mobility of electron cloud around a molecule
- ◆ Guiding principle – like dissolves like
 - ◆ If all three polarity dimensions match between solvent and solute we have high solubility



Emollient classes

- ◆ Hydrocarbons from mineral oils/petroleum
 - ◆ Mainly saturated hydrocarbons of more than 16 carbons long
- ◆ Fatty acids from animal and vegetable fats
 - ◆ Can be combined with natural or synthetic alcohols to esters
 - Mono-esters (typically isopropyl palmitate)
 - Di-esters (typically propylene glycol esters or adipic acid esters)
 - Tri-esters (typically triglycerides, vegetable oils)
 - Complex esters
- ◆ Fatty alcohols from petroleum or natural sources
 - ◆ Straight chain alcohols (typically cetearyl alcohol)
 - ◆ Guerbet alcohols (typically octyldodecanol)
- ◆ Silicones
 - ◆ Dimethicones
 - ◆ Cyclomethicones
 - ◆ Complex silicones and silicone polymers

Comparison of some liquid emollients


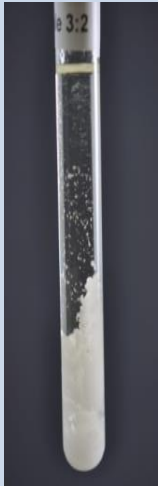





Liquid oil	Van der Waals interaction	Hydrogen bonding	Polarizability	
C12-15 Alkyl Benzoate	X	(X)	XX	Large polar group, highly polarizable
Octyldodecanol	X	X	X	Exposed hydrogen bonds
Isopropyl Palmitate	X	(X)	X	Medium polar, long FA chain, polarizable
Canola Oil	XX	(X)	X	Long chains, interacting with each other, low polar
Shea Butter Ethyl Esters	X	(X)	X	Long FA chains, exposed ester group, high polarizability
Mineral Oil	XX	-	-	Non polar, no hydrogen bonds, very strong Van der Waals
Dicaprylyl Carbonate	X	(X)	X(X)	Small molecule, more polar than other esters due to exposed carbonyl group and short chains

Hansen's Polarity Parameters

- Literature data and approximations

	VdW / Dispersive	Hydrogen bonding	Polarizability
Mineral oil	16.3	0	0
Cyclomethicone	12.9	1.3	1.0
Dimethicone	12.5	0.8	0.8
Canola Oil	17.5	3.3	4.1
Shea Butter Ethyl Esters	16.2	3.8	4.5
Skin	17.6	13.0	11.0
Glycerol	17.4	11.3	27.2
Water	15.5	16.0	42.3

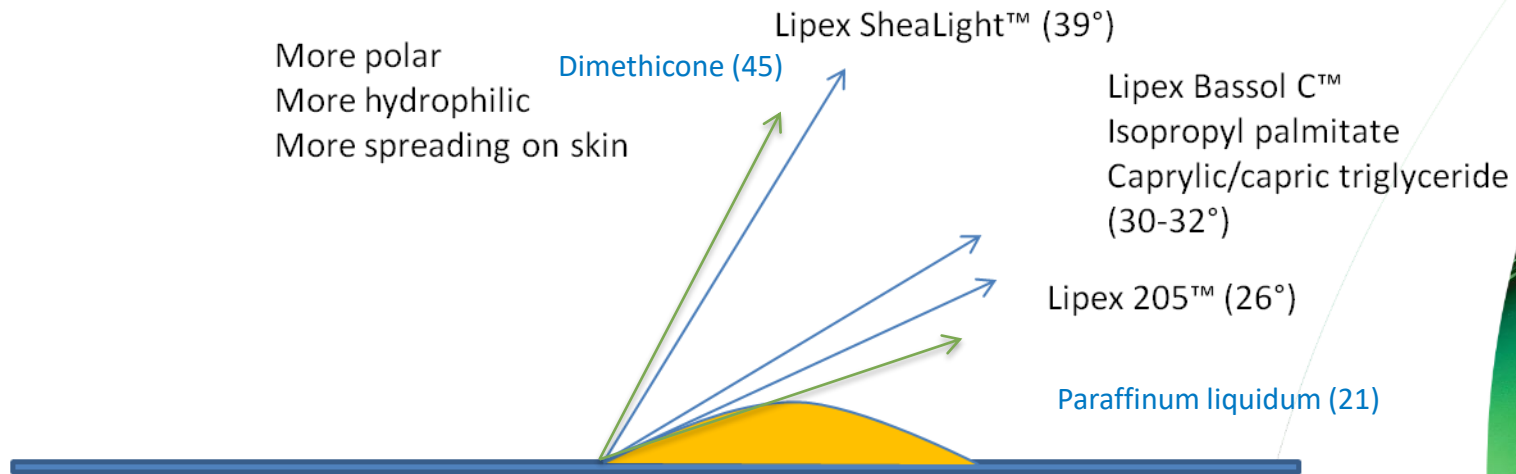
Shea Butter dispersed in various emollients (20% butter / 80% oil)

Canola Oil	Caprylic / Capric Triglyceride	Shea Butter Ethyl Esters	Dicaprylyl Ether	Isopropyl Isostearate	Paraffin Oil	Castor Oil
						

Lipex SheaLight™

(Shea Butter Ethyl Esters) is uniquely polar

- Contact angle on hydrophobic surface (teflon)

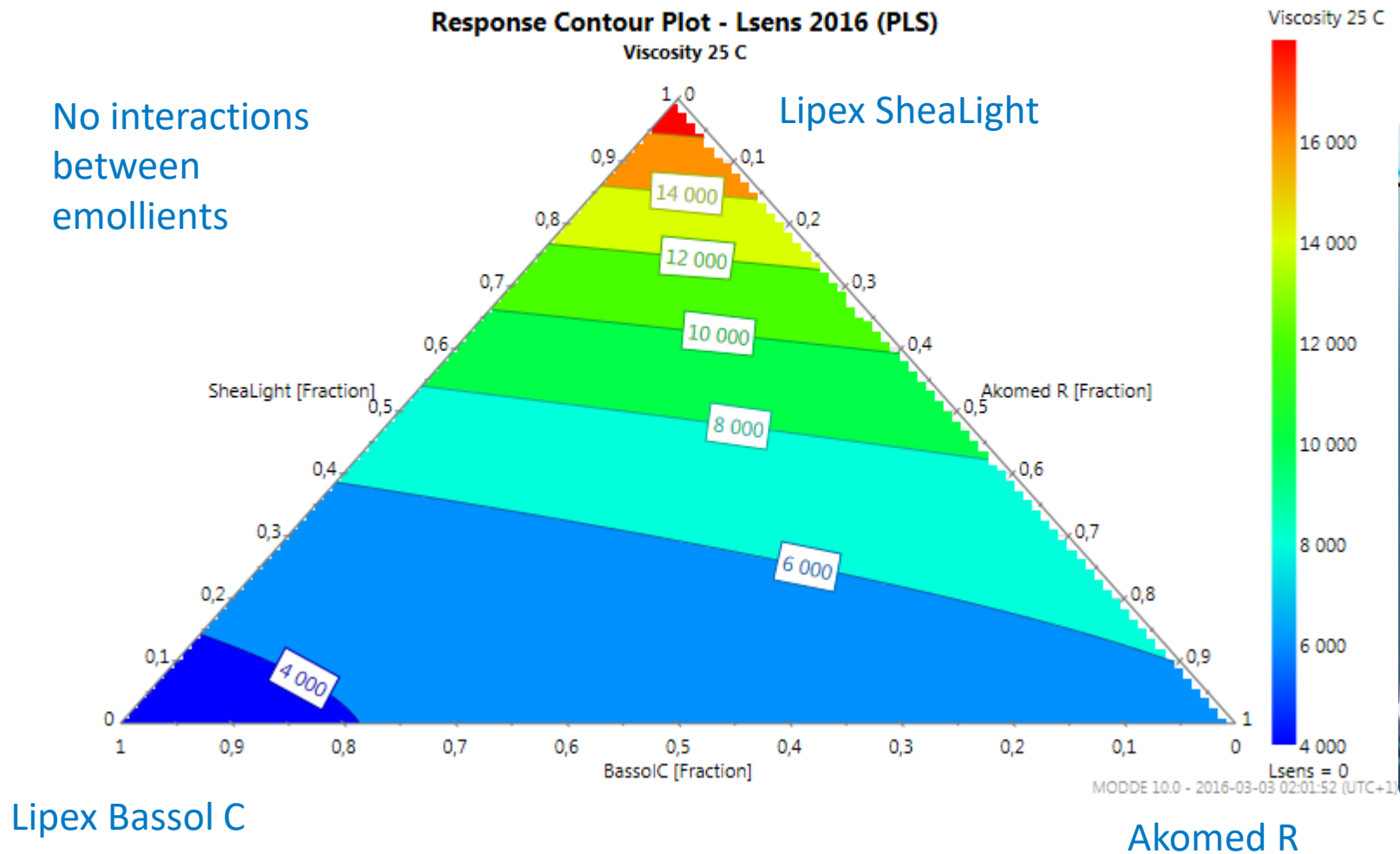


- Good spreadability on skin requires that emollient and skin polarity are matched
- Skin combines both hydrophilic and lipophilic properties -> balanced polarity is required

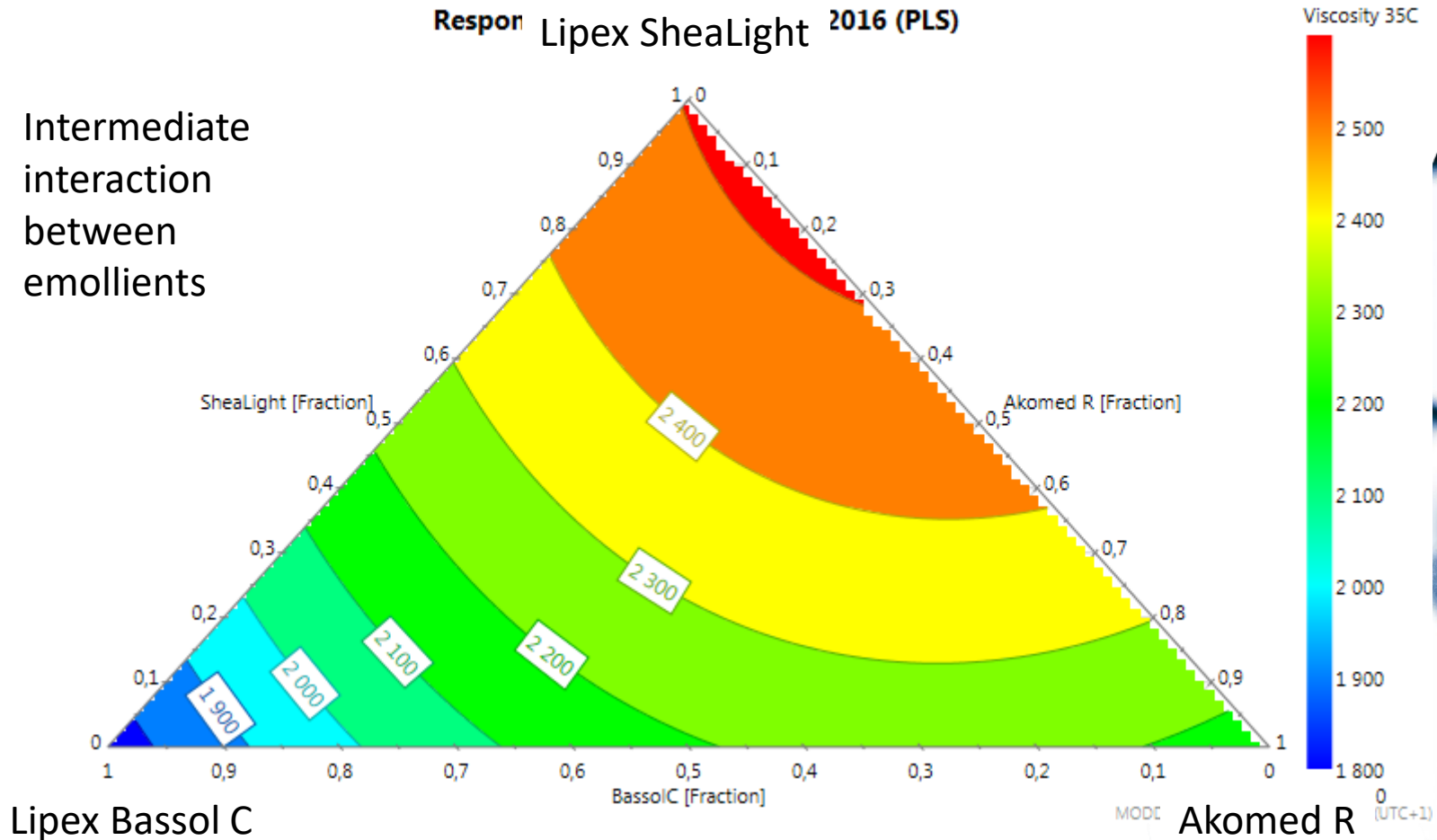
Example: Interaction between 3 emollients in a formulation

- ◆ Complex formulation but only emollient composition is changed
- ◆ Measurement of viscosity at three relevant temperatures 25, 35 and 45 C
- ◆ Emollients tested
 - ◆ Lipex SheaLight™
 - Low molecular weight, simple ester, low viscosity
 - ◆ Akomed R
 - Caprylic/capric triglyceride, intermediate molecular weight and polarity
 - ◆ Lipex Bassol C™
 - C18:1 based triglyceride, high molecular weight and viscosity, intermediate polarity
 - ◆ Tested in simple, model formulation, body lotion type

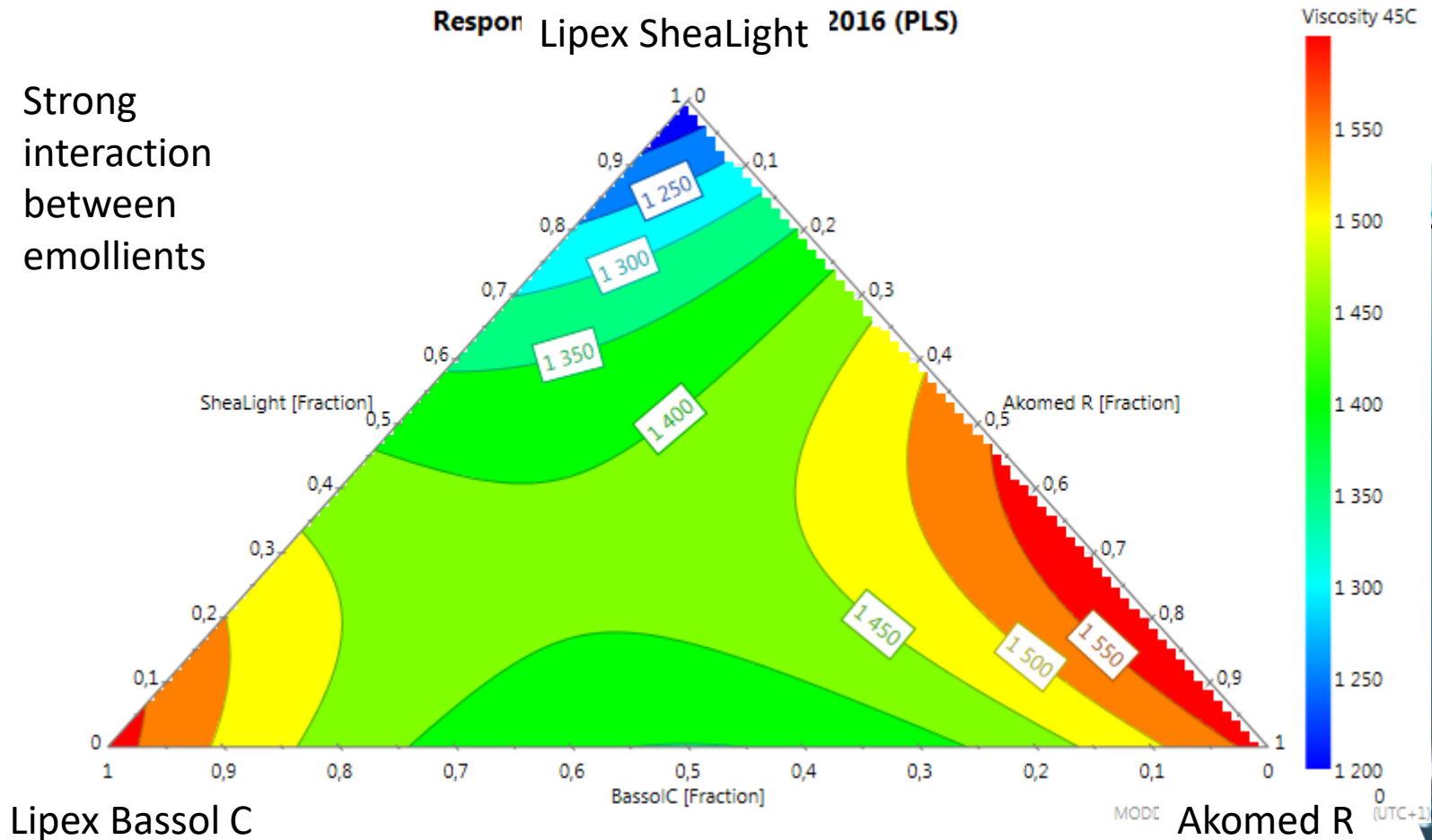
Viscosity at 25C as function of emollient composition



Viscosity at 35C as function of emollient composition



Viscosity at 45C as function of emollient composition



Conclusions

- ◆ Emollients offer great opportunities for optimising formulation rheology, stability and skinfeel
- ◆ Consider chemical structure and physical properties for finetuning application properties:
 - ◆ Polarity (molecular size, hydrogen bonds, polarizability)
 - ◆ Viscosity/rheology
- ◆ In complex emulsions, interactions often are more important than the effect of individual components
 - ◆ Do not evaluate emollients in pure form only as this will give incomplete information

