

Refractive Index Matching and Clear Emulsions

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Outlines

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- Physical Principles of RI Matching
- Cosmetic Applications
- Deviations and Practical RI Adjustment
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Introduction

Two ways of making clear emulsions

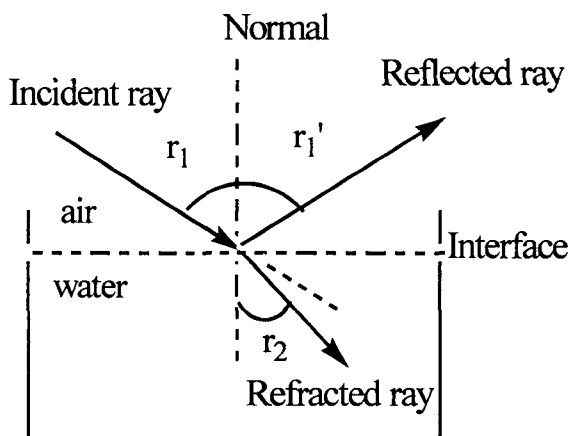
- Microemulsion

Visible light $\lambda = 400\text{-}700\text{ nm}$

Microemulsion, $d < 50\text{ nm}$

- Refractive Index Matching

Physical Principles of RI Matching



Law of Reflection

$$r_1 = r_1'$$

Law of Refraction

(Bending light ray)

$$n_1 \sin r_1 = n_2 \sin r_2$$

(Snell's Law)

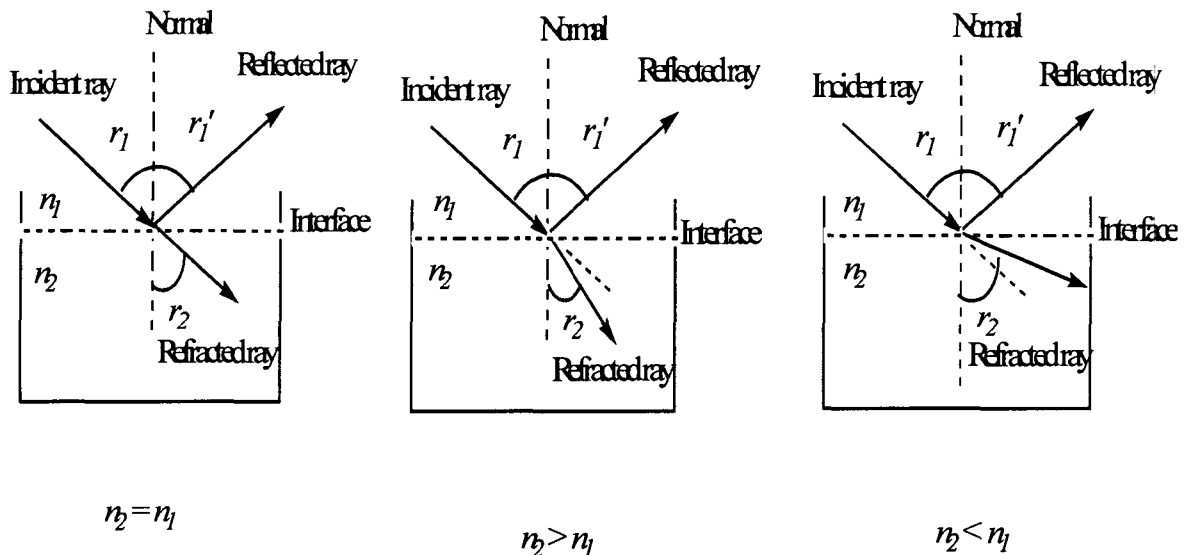
$$n = U_{\text{vac}}/U_{\text{sub}}$$

diamond, water, air

$$n : 2.419 \quad 1.33 \quad 1.003$$

$$n_1 \sin r_1 = n_2 \sin r_2$$

Three basic cases



RI of common ingredients (RT)

Ingredient	RI value (<i>n</i>)
Cyclomethicone and dimethicone (Dow Corning 1501)	1.3972
Cyclomethicone (KF 995)	1.3960
Cyclomethicone, phenyltrimethicone, dimethicone (Gelaid 5565)	1.4015
Cyclomethicone and dimethicone copolyol (Dow Corning 5225)	1.3975
Polyacrylamide, C13-14 isoparaffin, laureth-7 (Sepigel 305)	1.4460
Sodium acrylate/acryloyldimethyl taurate copolymer, isohexadecane, polysorbate 80 (Simugel EG)	1.4450
Hydroxyethylacrylate/sodium acryloyldimethyl taurate copolymer, squalane and polysorbate 60 (Simugel NS)	1.4475

RI of common ingredients (cont.)

Ingredient	RI value (<i>n</i>)
Glycerin	1.4680
Hexylene glycol	1.4276
Butylene glycol	1.4401
Propylene glycol	1.4355
Glycereth-7 (Liponic EG-7)	1.4720
PEG-6 (Carbowax PEG 300)	1.4615
PVP/VA Copolymer (Luviskol VA 73W)	1.4275
PVP (Luviskol K30, BASF AG)	1.3805

Concentration dependent RI of glycerin aqueous solution

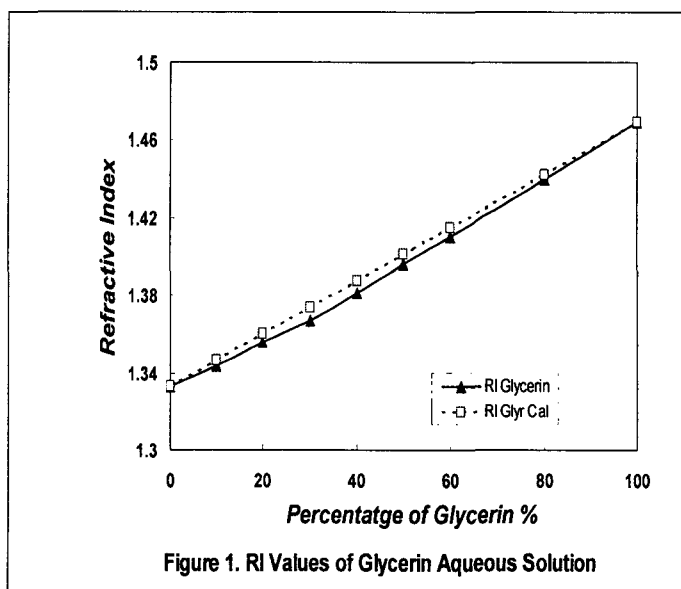
50% glycerin

50% water

$$\text{RI} = [1.468 + 1.330] / 2$$

$$= \mathbf{1.399}$$

Expt value = **1.396**



RI calculation equation

$$RI_{mix} = [W_1 \times n_1 + W_2 \times n_2 + W_3 \times n_3 + \dots + W_n \times n_n] / W_T \quad (1)$$

Where $W_T = W_1 + W_2 + W_3 + \dots + W_n$

(1) Simplified as:

$$RI_{mix} = [\sum(W_i \times n_i)] / W_T \quad (2)$$

Emulsion RI matching calculation equations

$$RI_{oil} = [\sum(W_i \times n_i)] / [\sum W_i] \quad (3)$$

W_i is a weight and n_i is RI value of each component in oil phase

$$RI_{water} = [\sum(W_i \times n_i)] / [\sum W_i] \quad (4)$$

W_i is a weight and n_i is RI value of each component in water phase

Formulation Limitations

1. Clear or close to clear oil and water phase
2. No reaction between ingredients in either phase.
10.0% glycolic acid
at pH = 3 $n = 1.3450$
at pH = 4 $n = 1.3555$
3. Ingredients should not have dual distribution in both phases
4. Make emulsions at room temperature

Skin care application, w/o AHA Gel

	Weight %	n
<i>Silicone oil phase</i>		
Dow Corning 1501(SF1214)	10.0	1.3971
Dow Corning 344(SF1204)	5.0	1.3942
Dow Corning 5225(SF1528)	10.0	1.3975
<i>AHA water phase</i>		
Water, deionized	35.5	1.333
Glycerin	27.0	1.468
Glycolic acid and arginine (AHCare G-60)	12.5	1.428

RI of AHA gel calculation

$$\begin{aligned} RI_{oil} &= (10 \times 1.3971 + 5 \times 1.3942 + 10 \times 1.3975)/25 \\ &= 1.3967 \end{aligned}$$

$$\begin{aligned} RI_{water} &= (35.5 \times 1.33 + 27 \times 1.468 + 12.5 \times 1.428)/75 \\ &= 1.3966 \end{aligned}$$

Characteristics of AHA gel

AHAs have been widely used in skin care formulations for **antiaging and antiwrinkle** effects.

Achieve a clear eye gel product with much **less irritation** by incorporating an AHA complex (glycolic acid and arginine) to form a w/o emulsion.

Hair care application, o/w PVP/VA gel

Ingredient	Weight %	<i>n</i>
<i>Silicone oil phase</i>		
Cyclomethicone (KF 995)	4.00	1.396
Cyclomethicone (and) phenyltrimethicone (and) dimethicones (Gelaïd 5565)	20.00	1.402
Polyacrylamide, C13-14 isoparaffin, laureth-7 (Sepigel 305)	3.00	1.446
<i>PVP/VA water phase</i>		
Water, deionized	26.50	1.333
Glycerin	21.35	1.472
PVP/VA copolymer (Luviskol VA 73W)	25.00	1.427
DMDM hydantoin (Glydant)	0.15	1.425

RI calculation of PVP/VA gel

$$RI_{oil} = (4 \times 1.396 + 20 \times 1.402 + 3 \times 1.446) / 27 \\ = 1.406$$

$$RI_{water} = (26.5 \times 1.333 + 21.35 \times 1.472 + 25 \times 1.427 \\ + 0.15 \times 1.425) / 73 \\ = 1.406$$

Characteristics of silicone PVP/VA clear gel

Combination of silicone and hair fixative ingredients PVP/VA or PVP

To deliver great shine, luxurious feel and manageability from silicone as well as styling function from the fixative resins to hair.

Expt. deviations from eq. 3&4

Expt. RI values deviate slightly from the calculated values.

Calculation of RI only applies for ideal solutions or ideally dilute solutions.

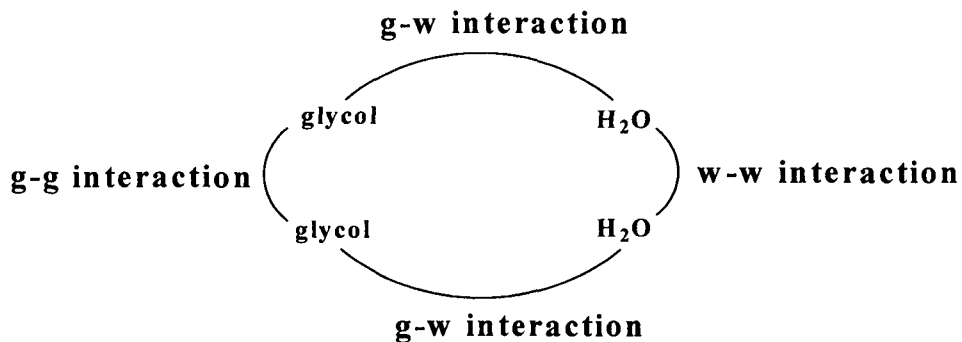
Precise calculations need to use chemical potential (μ_i), solute activities (a_i) and activity coefficients (γ_i).

RI Deviations in oil & water phase

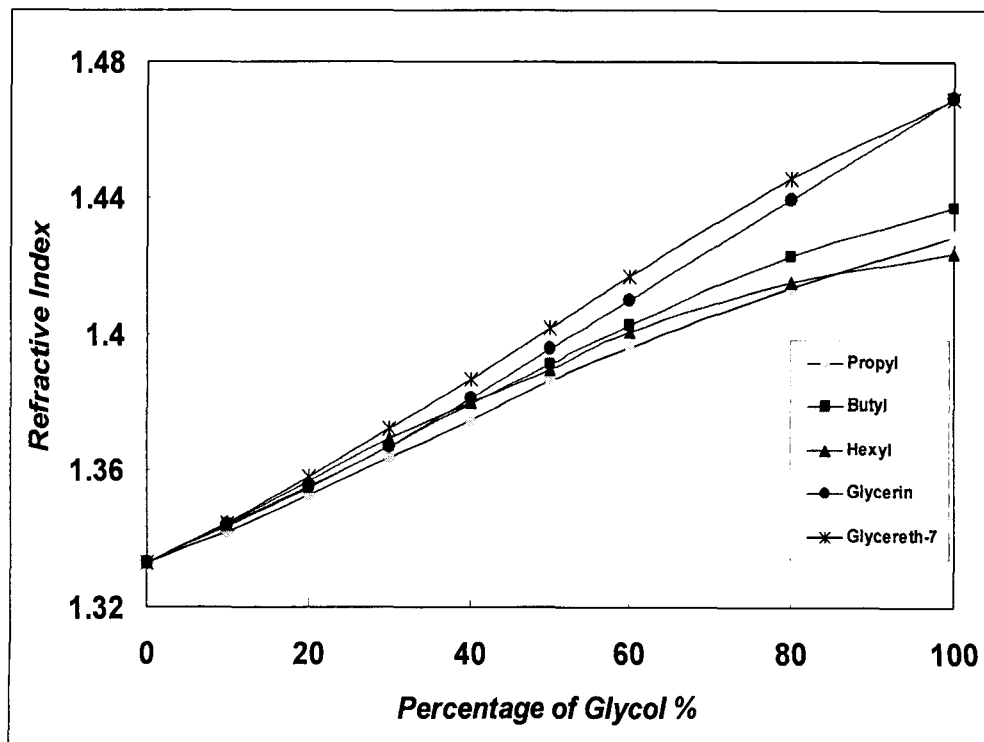
Very small deviation in the oil phase

Molecular structures of oil phase ingredients are similar so that molecular interaction between these ingredients is not very different.

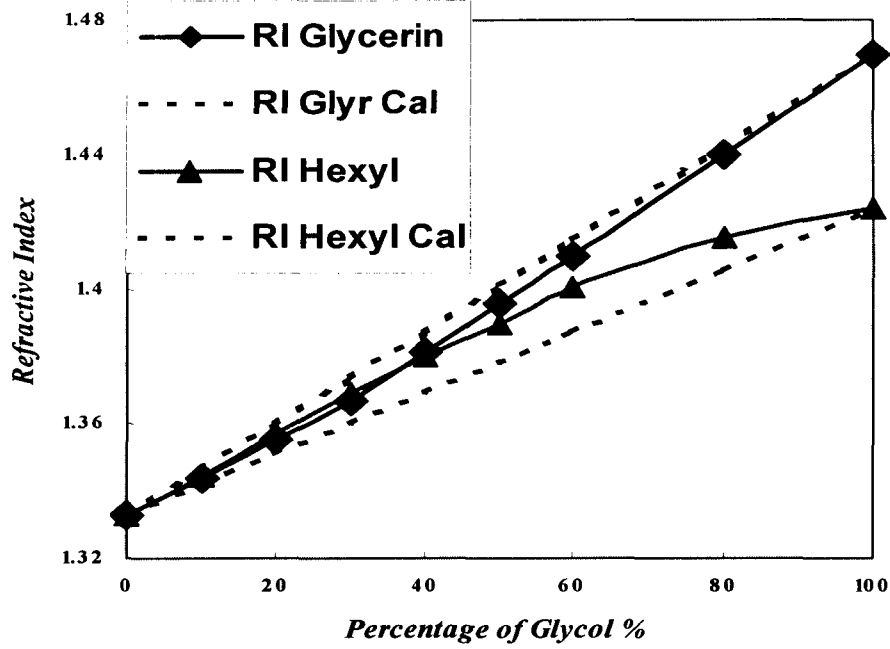
Very noticeable deviations in water phase



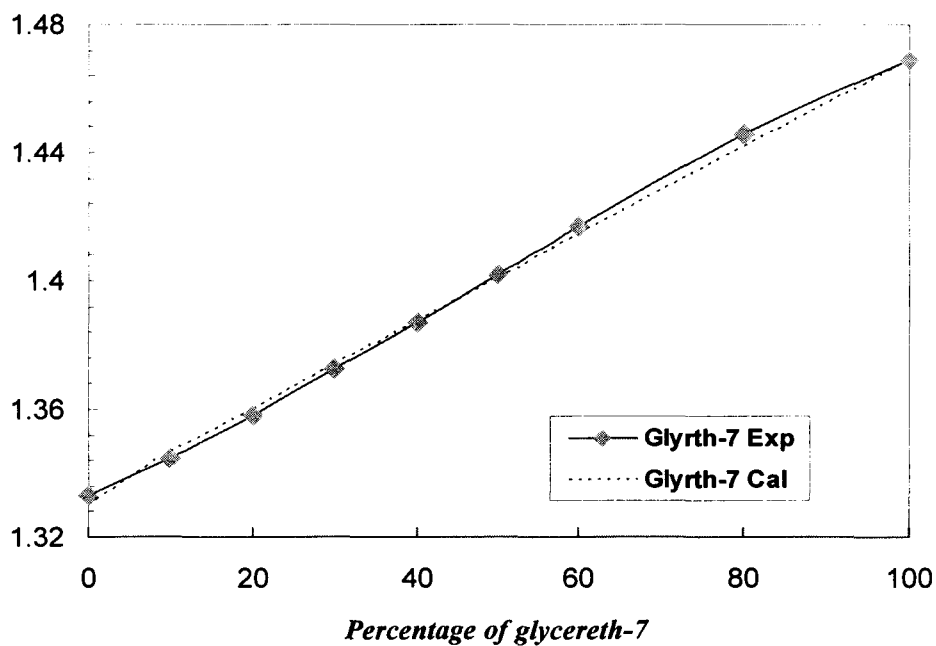
RI deviation in glycols solutions



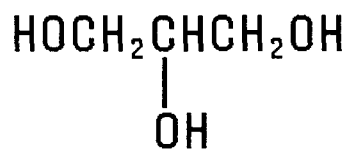
RI deviation of glycerin & hexylene glycol



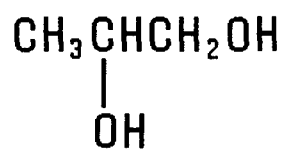
Concentration dependent slightly negative and positive deviation



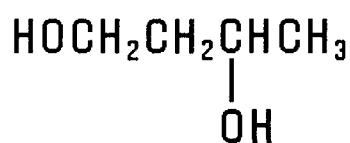
Structures of glycols



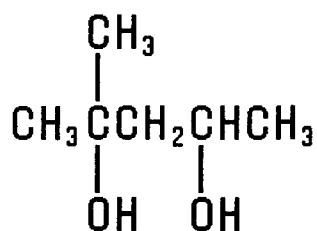
glycerin



propylene glycol



butylene glycol



hexylene glycol

Specific Gravity Change

50/50 solution SPG change

	SPG _{expt}	SPG _{cal}	Deviation	Dev.%
Glycerin	1.1268	1.1304	-0.0036	-0.32
H. Glycol	0.9870	0.9613	+0.0257	+2.67
B. glycol	1.0251	1.0085	+0.0166	+1.65
P. Glycol	1.0354	1.0184	+0.0170	+1.67

Conclusions

1. A calculation scheme has been developed for designing clear emulsion formulas by matching RI of water phase and oil phase.
2. RI matching can be used for skin care and hair care emulsion formulation.
3. Positive deviations and negative deviations were observed for water-glycol two-component systems.
4. Deviation originated from molecular interactions between glycol and water molecules. Specific gravity changes are observed along with deviations.
5. Use of index calculation scheme and deviation plots lead to more precise formulation design.

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