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Physiochemical Studies of Neutralizers and their Effects on Stability of Cosmetic Emulsion

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Abstract: Cosmetic emulsions were prepared using four different neutralizers; borax, sodium hydroxide, sodium carbonate and alkali extract from coconut husk (*Cocos nucifera*). The effectiveness of each of these materials as neutralizers/co-emulsifiers and as replacement for conventional neutralizer (borax) in cosmetic emulsions was evaluated by preparing samples of creams and lotions with these materials using a standard formulation. The samples were stored under ambient conditions and both microbial and physicochemical parameters were determined. The results obtained show that the materials are stable as alternative neutralizers/co-emulsifiers to borax in cosmetic emulsion preparations.

Key words: Neutralizers, cosmetic emulsion, physiochemical analysis, co-emulsifiers

Introduction

Recently in Nigeria, nearly 95% of the cosmetic products are derived from synthetic products (mineral oils). The object of the present study is based on the fact that all over the years, a lot of ingredients were employed and are still being employed for cosmetic preparations namely emulsifiers (stabilizer), dispersing agents emollients, pearling agent, plasticizers, neutralizing agents (co-emulsifier) etc.

Conventionally, borax is widely employed as the neutralizing agent in most cosmetic emulsions be it body creams lotions. The chemistry of borax reveals that on hydrolysis in water, 2 moles of sodium hydroxide and 4 moles of orthoboric acid are formed.

The need and search for cheaper source of raw materials as alternatives for conventional ones gave the impetus for this study. The study is therefore aimed at obtaining base line data which could act as spring board for further search and utilization of local and other raw materials in the cosmetic industry.

There is no doubt that we live in a culture that emphasizes physical beauty. We only need to look at images on television, magazine covers to realize that we are barraged with images of beauty perfection on a daily and sometimes hourly, basis. Intellectually, we know that media photographs today are digitally modified, but in our quest for perfection it is easy to forget.

Females are not alone in the subliminal exposure to super human physiques. In the jet age we now find ourselves, it is not only that the use of cosmetic is being abused, a lot of people are now going for cosmetic surgery. Nearly 90% of all cosmetic procedures are performed on women. Thompson *et al.* (1999) comments on the cultural impact on body image satisfaction in their text "Exalting Beauty". The synthetic cosmetic products not 100% safe. Some of the side effects have been well documented (Motwani *et al.*, 2002, Malhotra and Zatz, 2002; Tangarajan and Zatz, 2001; Zatz, 2000; Thompson, 1999; Phillips, 1991).

Uncontrolled uses of cosmetic have also resulted in some users finding themselves in psychiatric homes (Veale and Riley, 2001; Phillips, 1991). The primary object of this paper is to look for natural alternatives to these synthetic products.

Cosmetics as defined by the US Federal Food, Drug and Cosmetic Act 1938 as articles intended to be rubbed, sprinkle or sprayed on, introduced into, or otherwise applied to the human body or part thereof, for cleaning, beautifying, promoting attractiveness or altering the appearance of the body (Jellinek, 1995).

Oil-in-water emulsifying agents produced emulsions in which the continuous phase is hydrophilic, such emulsions are generally dispersible in water and conduct electricity. The surfactants which are capable of producing such emulsions usually have an hydrophile lipophile balance (HLB) of about 7. On the other hand, water in oil emulsifiers produce emulsions in which the continuous phase is lipophilic in character (oil, wax, fat etc.). These emulsions are not generally dispersible in water and do not conduct electricity. Such emulsions usually have an HLB of about 5.

For oil-in-water emulsion systems, certain emulsifiers predominantly lipophilic in nature are included to act as stabilizers, minimizing creaming and sedimentation, that is, they act as auxiliary emulsifiers or main emulsifiers as the case may be. Generally, materials which increase the thermodynamic stability and viscosity of the external phase of an emulsions also exert a stabilizing influence. Neutralizing agents and or co-emulsifiers function as stabilizers.

One of the most useful concepts developed for the control of the emulsion type by the selection of emulsifying agents is the hydrophile/lipophile balance (HLB) (Beans, 1972; Bloodfied, 1988; James, 1996; Sherman, 1967; Smart and Sponner, 1972). In such concept, surfactants are classified according to the size and strength of the hydrophilic and lipophilic portions of the molecules. However, the HLB system does not provide information as to the specific emulsifiers, or even the types of emulsifiers, that will produce the most stable emulsion. In the present study, we developed comparative studies on different neutralizers and co-emulsifiers as well as their effects on stability of cosmetic emulsions systems.

Table 1: Lotion cream fomulation LF (C1) and Lotion fomulation LF (L1) (Lloyd, 1962)

Component	Quantity (%)
LF (C1)	
Whiterex oil	7.89
Ritachol wax	4.03
Stearic acid	2.82
Hexadecanol	1.81
Petrolatum	0.81
Propyl paraben	0.10
Methyl paraben	0.10
Isopropyl myristate	0.60
Glycerine	0.81
Propylene glycol	1.21
Borax	0.41
Fragrance	0.60
Water	78.81
LF (L1)	
Whiterex oil	6.37
Ritachol wax	1.70
Stearic acid	1.23
Hexadecanol	1.32
Petrolatum	0.42
Propyl paraben	0.10
Methyl paraben	0.10
Isopropyl myristate	0.55
Glycerine	0.65
Propylene glycol	1.15
Borax	0.18
Fragrance	0.64
Water	85.59

LF (C1) Implies Literature fomulation with borax as neutralizing agent for the Cream (Lloyd, 1962), LF (L1) Implies Literature fomulation with borax as neutralizing agent for the Lotion (Lloyd, 1962)

Materials and Methods

Dried fruit bunch of *Cocos nucifera* were collected locally and burnt to ashes. The ash (3 g) was leached with hot distilled water and the solution was then filtered. The leaching was repeated until the residue was almost neutral to red limus paper. The extract was transferred into a 700 cm³ measuring cylinder and concentrated by evaporation to 250 cm³ in volume. A 0.12M HCl was then titrated against 25 cm³ of the extract using methyl orange as indicator. Molarity of the carbonate in the ash extract was then obtained from the volumetric analysis.

Preparation of Sample Creams

Cream formulation (CF) and Lotion formulation (LF) were prepared using the method developed by Lloyd (1962).

All the components were weighed in accordance with the percentages stated. The oil soluble components were weighed into a beaker while the other water soluble components were separately weighed into another beaker. The two beakers were heated in a hot plate to attain the desired temperature (70°C) with the phase to be poured at a relatively higher temperature (75°C) to enhance cooling *in situ*. After attaining the desired temperatures, the phases were run into a mixing vessel. The oil soluble component was run into the water soluble components while stirring with the homogeniser to ensure proper emulsification. The mix was further cooled to 45°C before perfuming and then transferred to cans.

Table 2: Cream and lotions derived from the other neutralizers (Lloyd, 1962)

Components	Quantity (%)		
	C2	C3	C4
Creams			
Whiterex oil	7.89	7.89	7.89
Ritachol wax	4.03	4.03	4.03
Stearic acid	2.82	2.82	2.82
Hexadecanol	1.81	1.81	1.81
Petrolatum	0.81	0.81	0.81
Propyl paraben	0.10	0.10	0.10
Methyl paraben	0.10	0.10	0.10
Isopropyl myristate	0.60	0.60	0.60
Glycerine	0.81	0.81	0.81
Propylene glycol	1.21	1.21	1.21
Neutralizer	0.01	0.18	0.19
Fragrance	0.60	0.60	0.60
Water	79.21	79.04	79.03
Lotion			
Whiterex oil	6.37	6.37	6.37
Ritachol wax	1.70	1.70	1.70
Stearic acid	1.23	1.23	1.23
Hexadecanol	1.32	1.32	1.32
Petrolatum	0.42	0.42	0.42
Propyl paraben	0.10	0.10	0.10
Methyl paraben	0.10	0.10	0.10
Isopropyl myristate	0.55	0.55	0.55
Glycerine	0.65	0.65	0.65
Propylene glycol	1.15	1.15	1.15
Neutralizer	0.004	0.004	0.004
Fragrance	0.64	0.64	0.64
Water	85.77	85.69	85.68

C2 (cream derived from Sodium hydroxide), C3 (cream derived from Sodium carbonate), C4 (cream derived from local ash alkali extract), L2 (lotion derived from Sodium hydroxide), L3 (lotion derived from Sodium carbonate), L4 (lotion derived from local ash alkali extract)

The same procedure was repeated using the other neutralizers: sodium hydroxide, sodium carbonate and local ash as shown in Table 1 and 2. The mixing speed was generally 240 rpm for the first two minutes and later at a reduced speed of 50 rpm while cooling until the emulsion attained a temperature of 45°C.

Physicochemical Analysis

Various physicochemical analysis such as pH determination, conductivity test, specific gravity, viscosity, thermal stability test water loss/other physical test were carried out on the samples.

Free Alkali Test

Free alkali in emulsions usually consists of hydroxide and carbonate of sodium, potassium or both. Free alkali is the hydroxide and is usually expressed as Na₂O. The sample (cream/lotion) weighing 5 g was placed in a 250 mL flask. The samples were dissolved in 100 mL water by warming gently. The resultant solution was cooled to room temperature, 3 drops of 0.1% methyl orange indicator was added and titrated with 0.05M H₂SO₄ solution.

Calculation

$$\text{Free alkali (expressed as Na}_2\text{O)} = \frac{V \times 100 \times 0.0031\%}{W}$$

Where

V = Volume (mL) of 0.05 M H₂SO₄ solution and

W = Weight (g) of the sample

Results and Discussion

Results of samples based on physical observation of emulsion formation, surface appearance, water loss and percentage yield are shown in Tables 3-5.

The obvious difference between the four series of neutralizers was that whereas spontaneous emulsification was noticed when borax and caustic soda were used as neutralizers, emulsification was quite slower in the case of sodium carbonate and local ash extract. Again foaming during manufacture was moderate in the case of borax and caustic soda as neutralizers than sodium carbonate and local ash were as neutralizers. Consequently more firm creams/lotions were produced from the borax/fatty acid and soda/fatty acid interactions than the soft creams/lotions formation when sodium carbonate and local ash extract were used as neutralizer/co-emulsifiers.

Results obtained with regards to water loss when stored in petri dishes and surface examination showed that the rate of evaporation of water from emulsions derived from borax and caustic soda were quite slower than emulsions derived from Sodium carbonate and local ash alkali extract probably due to their oily nature.

Table 5 further elucidates the rate of water loss on emulsion samples with time. Though it looks obvious that prolonged exposure leads to an increase in the rate of evaporation of water from the emulsion samples, the observed or noticeable decrease from days 5 and above indicates that the linearity is not absolute. The reason for the subsequent decrease might be due to possible exhaustion of the non absorbed water on the emulsion system.

As might be expected, the rate of water evaporation from lotions were not as sharp as might be anticipated when compared to those of creams. This might be due to the fact that much of the water is strongly bound to the emulsion system and consequently did not exist as moisture (Lloyd, 1962).

Table 3: Emulsion formation of creams/lotions during manufacture

Samples	Observation		
	Rate of formation	Type of cream	Foaming propensity
C1	Spontaneous	Firm	Minimum
L1	Spontaneous	Slightly soft	Minimum
C2	Spontaneous	Firm	Moderate
L2	Spontaneous	Soft	Moderate
C3	Not spontaneous	Transparent	Poor
L3	Not spontaneous	Soft	Poor
C4	Not spontaneous	Soft	Poor
L4	Not spontaneous	Soft	Poor

Tables 4: Surface examination of creams/lotions and yield (%)

Samples	Yield (%)	Nature of surface						
		24 h	48 h	72 h	96 h	120 h	144 h	168 h
C1	98.05	V.G	V.G	V.G	V.G	V.G	V.G	V.G
L1	98.50	V.G	V.G	V.G	V.G	V.G	V.G	V.G
C2	98.10	V.G	V.G	V.G	V.G	V.G	V.G	V.G
L2	98.70	V.G	V.G	V.G	V.G	V.G	G	G
C3	97.80	G	F.G	F.G	F.G	F.G	M	M
L3	97.90	G	G	F.G	F.G	F.G	F.G	M
C4	97.60	F.G	F.G	F.G	F.G	M	M	M
L4	97.65	F.G	F.G	F.G	F.G	F.G	F.G	M

VG = Very Glossy, FG = Fairly Glossy, M = Matt (dull surface)

Table 5: Water loss in mg/5 g of sample

Cream/Lotion	24 h	48 h	72 h	96 h	120 h	144 h	168 h
C1	1.9	2.5	3.2	3.5	5.3	5.8	6.70
L1	2.1	3.5	5.1	6.3	8.3	9.4	9.40
C2	3.8	4.7	6.5	8.1	9.0	10.05	10.50
L2	4.0	4.8	6.2	7.9	9.5	10.70	11.25
C3	5.0	6.2	7.5	8.9	10.3	11.50	11.75
L3	5.5	6.7	7.8	9.1	10.5	13.9	14.25
C4	5.3	6.5	8.0	9.2	10.8	11.50	12.10
L4	5.7	6.8	8.5	9.6	11.0	11.80	12.35

Table 6: Specific gravity and viscosity measurements

Sample	Specific gravity						Viscosity (in poises)							
	1 ¹	1	2	3	4	5	6	1 ¹	1	2	3	4	5	6
C1	1.30	1.35	1.35	1.36	1.35	1.35	1.35	13.90	14.10	14.10	14.15	14.10	14.10	14.10
L1	1.05	1.10	1.10	1.10	1.15	1.10	1.10	7.30	7.35	7.35	7.36	7.37	7.35	7.35
C2	1.25	1.30	1.31	1.30	1.30	1.28	1.29	13.60	13.80	13.80	14.05	14.10	14.00	14.00
L2	1.02	1.05	1.05	1.05	1.05	1.01	1.01	7.20	7.30	7.30	7.30	7.30	7.22	7.22
C3	1.20	1.21	1.21	1.22	1.22	1.21	1.21	13.40	13.50	13.50	13.52	13.51	13.44	13.43
L3	0.980	0.990	0.990	0.985	0.985	0.970	0.965	6.95	9.95	6.95	6.95	6.95	6.75	6.76
C4	1.18	1.21	1.21	1.21	1.21	1.20	1.20	12.45	12.45	13.00	13.10	13.22	13.10	13.12
L4	0.960	0.970	0.975	0.976	0.976	0.971	0.971	6.80	6.80	6.85	6.91	6.91	6.85	6.86

Table 7: Results of thermal stability and separation tests

Sample	Thermal stability (% Separation)						Separation test (% Separation)					
	1	2	3	4	5	6	1	2	3	4	5	6
C1	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	0.50	0.55	0.15	0.10
L1	Nil	Nil	Nil	-	-	-	0.10	0.15	0.10	0.10	0.15	0.15
C2	Nil	Nil	Nil	-	-	-	Nil	Nil	Nil	0.10	0.20	0.25
L2	Nil	Nil	Nil	-	-	-	Nil	Nil	Nil	0.10	0.25	0.30
C3	Nil	Nil	Nil	-	-	-	-	0.20	0.30	0.25	0.25	0.35
L3	Nil	Nil	Nil	-	-	0.15	0.20	0.25	0.30	0.35	0.35	0.30
C4	Nil	Nil	Nil	0.10	0.20	0.20	-	0.25	0.20	0.25	0.35	0.30
L4	Nil	Nil	Nil	0.25	0.50	0.50	0.20	0.30	0.45	0.45	0.45	0.55

The rate of water evaporation from cream or lotion is not an index of stability. Surface examination reveals that emulsions derived from borax and caustic soda were more glossy when compared to those derived from sodium carbonate and local ash extract. Disregarding the effect of dyes and pigments, the appearance of an emulsion is determined by the particle size of the dispersed droplets and the difference in the refractive indexes of the two phases. The more emulsified an emulsion system, the smaller the particle size and the more transparent (glossy) or increase in opacity the emulsion would be (Lloyd, 1962, Kirt-Othmer, 1985).

The difference in yield between borax, sodium hydroxide, sodium carbonate and local ash alkali extract emulsions could be attributed to the above reasons and also to the slower rate of emulsification as observed with the case of the later (Table 1).

Physicochemical Analysis

Instability in cosmetic emulsion can manifest by changes in rheological properties including separation or breaking down, pH change and decolouration. Consequently, a number of physicochemical parameters were employed in these studies for a period of six months and variations in results obtained were used as a mark of stability or instability as the case may be with the respective emulsions under study in the same environmental condition.

Emulsions made with borax were essentially that of Oil-in-water (OW) type emulsions. Emulsions made with caustic soda were equally oil-in-water type emulsions except for a few discrepancies. As can be seen above, phase inversion occurred for creams/lotion based on caustic soda, sodium carbonate and local ash extract.

Free Alkali and Acid Rancidity Test

Two methods were employed for the determination of free alkali/acidity of the emulsion samples.

Free acidity values obtained with sodium carbonate and local ash extract emulsions ranged between 0.95-1.20% with negligible values of free alkali content. This could be due to insufficient amount of alkali necessary to neutralize the free fatty acid of the oil phase.

In monitoring cosmetic emulsions, significant variation in the values of free alkali or acidity from its initial value after manufacture could be due to microbial proliferation. Consequently, a stable product is one which shows no significant changes in its physicochemical characteristics during storage with extrinsic factors which promotes degradation being well guided against.

Rancidity test was carried out on the various samples immediately after manufacture and thereafter six months later. The results show no trace of incipient rancidity on any of the samples. Consequently, any significant changes in the values of the emulsion samples under study may not have been due to rancidity.

Results in Table 6 show that the specific gravity of the emulsion samples is not appreciably different from its original values within the six months monitoring period except in few cases which may be attributed to phase inversion.

Also viscosity measurement using the Lloyds method (1962) gave reproducible results. In general, change in specific gravity and viscosity of an emulsion are used as stability parameters. Although many emulsions appear to be stable for a relatively length of time, they are not stable in strict thermodynamic sense of the word. An increase in emulsifying agent concentration can increase viscosity by increasing the effective volume of the globules and their rigidity or by increasing the viscosity of either the internal or the external phase. According to Lloyd (1962), a more uniform emulsion has a higher viscosity than emulsions having a broad droplet size range.

Thermal stability test for the emulsion samples were generally high except for L3, C4 and L4 while separation test results were equally high (Table 7). The upper limit permissible for a stable emulsion under these two tests is 1% (NIS/SON). Consequently, all the samples within the period of

studies were intrinsically stable. Generally an important requirement for accelerated ageing tests for predicting stability is that they should merely speed up the processes whereby instability occurs under normal storage conditions.

Conclusions

Physicochemical studies of neutralizers and their effects on stability of cosmetic emulsion have been achieved through the use of locally available raw materials. The materials which increase the thermodynamic stability and viscosity of the external phase of the emulsions also exert a stabilizing influence.

References

- Beans, H.S., 1972. Preservatives for pharmaceuticals. *J. Cosmet. Chem. Great Britain*, 24: 120-128.
- Bloodfied, D., 1988. *Microbial Quality Assurance in Pharmaceuticals, Cosmetics and Toiletries*. Chichester Ellis Harwood, London, 210.
- James, M.J., 1996. *Modern Food Microbiology*, 2nd (Edn.), D. Van Nostrand Company, New York, pp: 75.
- Jellinek, J.S., 1995. *Formulation and Function of Cosmetic*. John Wiley and Sons. New York, pp: 45.
- Kirt-Othmer, O., 1985. *Concise Encyclopedia of Chemical Technology*. 3rd Edn., 24: 325.
- Lloyd, I.O., 1962. *Surface Chemistry: Theory and Industrial Applications*. ACS Monograph 153, Reinhold Pub. Co. New York.
- Malhotra G.G. and J.I., Zatz, 2002. Investigation of nail permeation enhancement by chemical modification using water as a probe. *J. Pharm. Sci.*, 91: 312-323.
- Motwani, M.R., L.D. Rhen and J.L. Zatz, 2002. Influence of vehicles of on the phase transitions of model Sebum. *J. Cosmet. Sci.*, 53: 35-42.
- Phillips, K.A., 1991. Body dysmorphic disorder; the distress of imagined ugliness. *A.M.J. Psychiatry* 148: 1138-1139.
- Sherman, P., 1967. Accelerated testing of emulsion stability. *J. Colloid Interface Sci.*, 24: 190-210.
- Smart, R. and D.F. Spooner, 1972. Microbiological spoilage in pharmaceuticals and cosmetics. *J. Cosmet. Chem.*, 23: 721-737.
- Tangarajan, M. and J.L. Zatz, 2001. Kinetics of permeation and metabolism of α -tocophenol and α -tocophenol acetate in micro-yucatan pig skin. *J. Cosmet. Sci.*, 52: 35-50.
- Thompson, J.K., I.J. Heinberg, M. Altabe and S. Tantleff-Dun, 1999. *Exacting beauty; Theory, assessment and treatment of body image disturbance*. Washing DC: Am. Psychol. Assoc.,
- Veale, D. and S. Riley, 2001. Mirror, mirror on the wall, who is the ugliest of them all? The psychopathology of mirror gazing in body dysmorphic disorder. *Behavioral Res. Ther.*, 39: 1381-1393.
- Zatz, J.L., 2000. Optimizing skin delivery. *Cosmet. Toil.*, 115: 31-35.