International Journal of Pharmaceutical Research and Applications
Volume 11, Issue 1 Jan - Feb 2026, pp: 703-712 www.ijprajournal.com ISSN: 2456-4494

Nanoemulsion-Based Sunscreens: A Review on Formulation Methods, Evaluation and Photoprotection

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Date of Submission: 25-01-2026 Date of Acceptance: 05-02-2026

ABSTRACT
Sunburn, skin ageing and skin cancer are all primarily caused by ultraviolet (UV) radiation, particularly UVA and UVB rays. Despite their widespread use, conventional topical sunscreens frequently have drawbacks such as low stability, inconsistent UV filter distribution, and inferior cosmetic qualities. Sunscreens based on nano-emulsions have become a sophisticated formulation strategy to deal with these issues. Transparent or translucent systems with droplet sizes ranging from 5 to 200 nm, known as nano-emulsions, improve the uniform distribution and efficacy of UV filters on the skin. In order to lower interfacial tension, oil and aqueous phases are combined with appropriate surfactants and co-surfactants to create nano-emulsion sunscreens. Both low-energy procedures, like cold emulsification, and high-energy methods, are used. Better film development on the skin and a large increase in SPF are provided by the better distribution of UV filters in nanoemulsions. Superior cosmetic benefits are also provided by nanoemulsion sunscreens, which have a translucent appearance. But issues like rising production costs and skin penetration-related regulatory worries still exist. With continued research concentrating on sustainable substitutes such Pickering emulsions to enhance safety and environmental compatibility, nanoemulsion technology offers a major leap in sunscreen composition overall.
Keywords: Nanoemulsion, Sunscreens, Photoprotection

I. INTRODUCTION

The dangerous solar radiation is made up of three types of ultraviolet (UV) radiation: UVA, UVB, and UVC. UV C light is not very hazardous to skin since it is filtered by the ozone layer before reaching the earth's surface. Sunburn is caused by UVB radiation, which destroys the skin. [1] UVA radiation reaches the deeper layers of the dermis and epidermis, causing the skin to age prematurely. UV exposure has been related to an increased risk of skin cancer. [2] UV filter materials (sunscreens) are classified as UVA, UVB, and broad-spectrum protection filters according to their capacity to absorb shorter or longer wavelengths. The most prevalent technique of avoiding UV-induced skin damage is using topical sunscreen.[3]

Nanoemulsion is a transparent, translucent oil-water emulsion stabilised by a surfactant film layer. [4] Surfactants play an important role in nanoemulsion formulations because they can dissolve lipophilic active substances such as Tween 80. Cosurfactants are essential to help lower interfacial tension because surfactants alone are insufficient to reduce water and interfacial tension. [5] In addition to reducing interfacial tension between water and oil, cosurfactants make the interface more fluid, which may increase the system's entropy. Nanoemulsions have incredibly small droplet sizes, ranging from 5 to 200 nm. To make nanoemulsions, surfactants and cosurfactants are used to reduce interfacial tension between the oil and water phases.[6]

Numerous investigations have shown that nanoemulsions can increase effectiveness and prevent creaming and other emulsion degradation caused by storage. Nanoemulsions are increasingly being used in cosmetic products due to their desirable physical characteristics, which include small droplet size with large interfacial area, transparent and clear appearance, high solubility capacity, low viscosity, and high kinetic stability because this type of formula prevents sedimentation and flocculation. [7]

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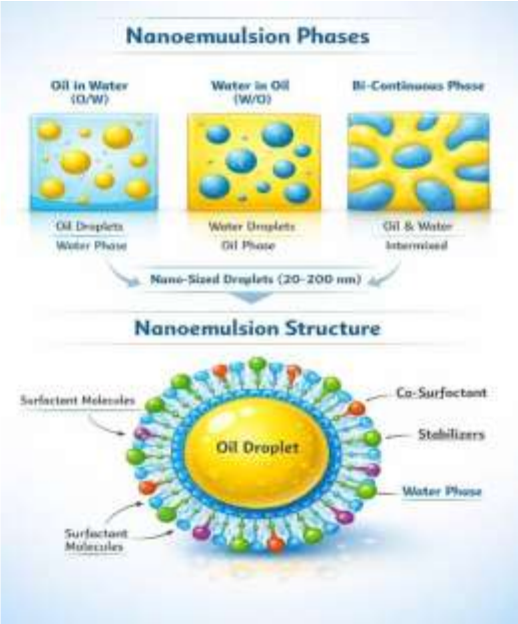

Fig 1 Nanoemulsion Structure

Additionally, nanoemulsion systems have been employed to enhance the solubility and deposition of synthetic UV filters such as bemotrizinol (BEMT), resulting in improved photostability and SPF performance. [8]

II. ADVANTAGE OF NANOEMULSION SUNSCREEN CREAM [9] [10] [11] [12]

- Enhanced UV protection.
- Nanoemulsions enhance UV filter dispersion, resulting in more uniform and effective UVA/UVB protection
- By increasing the dispersion of UV filters, nanoemulsions offer more consistent and potent defence against UVA and UVB radiation. • Improved skin penetration
- At lower doses, very small droplet sizes increase sunscreen efficacy by improving penetration into the stratum corneum.
- Nanoemulsions are thermodynamically stable, preventing creaming, flocculation, and phase separation.
- Improved Bioavailability of Actives.

III. DISADVANTAGES OF NANOEMULSION SUNSCREEN CREAM [13][14][15]

- Potential Skin Penetration Risk
- Nanoparticles may penetrate deeper skin layers, raising concerns about systemic absorption and long-term safety.
- Requires specialized equipment (high-pressure homogenizers, ultrasonication), increasing formulation cost.
- stricter regulatory scrutiny in many countries.
- Nanoemulsions can be sensitive to temperature and pH variations.

IV. MATERIALS AND METHODS

4.1 Materials:

Table 1 Composition of Nanoemulsion

S.NO	MATERIALS	IMPORTANCE	EXAMPLES
1.	Oilphase[16]	Solubilizes lipophilic activeing redients and forms the dispersed phase	Coconut oil, olive oil, sunflower oil, is opropylmyristate, essential oils[nutmeg oil]
2.	Surfactant[17]	Reduces interfacial tension and stabilizes nano sized droplets	Tween 20, tween 80, span 20, span 80
3.	Cosurfactant[18]	Enhances flexibility of interfacial film and improves nanoemulsion stability	Propylene glycol, PEG 400, ethanol, glycerol

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4.	Aqueousphase[19]	Acts as continuous phase in O\W nanoemulsions.	Purified water, Distilled water.
5.	Preservatives[20]	Prevents microbial growth and increases shelf life.	Methyl paraben, propyl paraben, henoxyethanol.
6.	Antioxidants[21]	Prevents oxidation of oil and active ingredients	Vitamin E, BHT, Ascorbic acid.
7.	pHadjusters\Buffers[22]	Maintains formulations pH and Skin compatibility	Citric acid, Sodium hydroxide, Phosphate buffer.
8.	Stabilizers\Thickening agents(optional)[23]	Improves Viscosity and physical stability.	Carbopol, Xanthangum, HPMC.

4.2 METHODS
4.2.1 PREFORMULATION: [24] [25] [26]

Preformulation studies are important preparatory investigations conducted prior to the development of a nanoemulsion. These investigations aid in identifying appropriate excipients, optimising formulation factors, maintaining stability, and increasing drug bioavailability.

- **Solubility Studies: [24]**

To assess the drug's solubility in different oils, surfactants, and co-surfactants. Add surplus medicine to 2-3 mL of your preferred oil, surfactant, or co-surfactant. Seal the vial and mix with a vortex mixer. Store samples at 25 ± 2°C for 48-72 hours. Centrifuge at 3000 RPM for 15 minutes. Analyse the supernatant with a UV-visible spectrophotometer or HPLC.

- **Oil Phase Selection: [24]**

To find an oil capable of dissolving the most medicine and generating a stable nano emulsion, do solubility tests in several oils (e.g., medium-chain triglycerides, oleic acid, castor oil). Examine medication solubility and miscibility. Oil with the highest solubilisation capacity is selected.

- **Selection of Surfactants: [24]**

Choose a surfactant with excellent emulsification efficiency. Mix oil and surfactant in a 1:1 ratio. Gently whisk in the mixture drop by drop into the distilled water. Check for clarity and the number of required Inversions.

- **Selection of Co-surfactants: [25]**

To make the interfacial film more flexible and lower interfacial tension. Make oil + surfactant + co-surfactant combinations. Dilute with water and check the transparency and stability.

- **Pseudo-Ternary Phase Diagram Construction: [25]**

To determine the nano-emulsion area. Make Smix (surfactant:co-surfactant) in 1:1, 2:1, and 3:1 ratios. Titrate with water dropwise after mixing oil and Smix in various ratios. Examine phase behaviour and transparency.

- **Study of Compatibility (Drug–Excipient Interaction) [25]**

To assess the drug's and excipients' chemical compatibility. Combine the medication with the excipients. Use XRD, DSC, or FTIR analysis. Compare the pure drug's spectra and thermograms.

- **Calculating the Critical Micelle Concentration (CMC) [26]**

To ascertain the lowest concentration of surfactant needed to produce micelles. Make increasingly concentrated surfactant solutions. Determine the conductivity or surface tension. Plot the concentration vs the measured parameter.

- **Test for Emulsification Efficiency [26]**

Add a predetermined amount of the oil-surfactant mixture to water to assess the surfactant's emulsifying capacity. Determine how many flask inversions are required to achieve homogeneity.

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Use a UV spectrophotometer to measure transmittance.

4.2.2 FORMULATION:

I. High-Energy Techniques [27]

Large disruptive forces are produced in high-energy methods by the employment of mechanical devices such as ultrasonicators, microfluidizers, and high pressure homogenisers that generate microscopic droplets. The size of the droplets is determined by the equipment, production parameters such as temperature and time, and the sample's qualities and composition. High-energy procedures are costly due to their need for specialised equipment and high energy consumption.

- **High Pressure Homogenization: [28]**

It is the most prevalent method for producing nanoemulsions. This approach uses a high- pressure homogeniser or a piston homogeniser to produce nanoemulsions with particle sizes of up to 1 nm. During the process, the macroemulsion is driven through a tiny orifice at an operating pressure ranging from 500 to 5000 psi. Because of the process, multiple factors such as hydraulic shear, severe turbulence, and cavitation work together to produce extremely small droplet sized nanoemulsions.

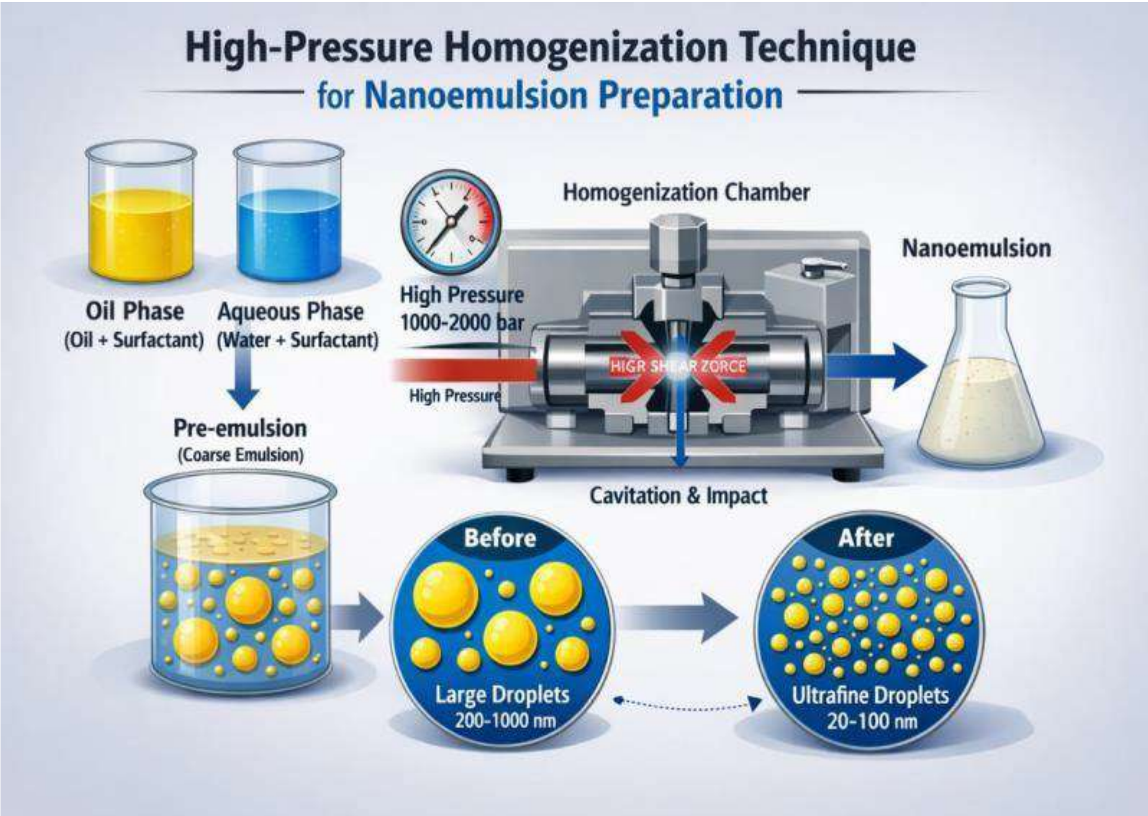

Fig 2 High Pressure Homogenization Technique

- **Ultrasonication Method: [29]**

In ultrasonic emulsification, energy is supplied using so-called sonotrodes, which include piezoelectric quartz crystals that may expand and contract in response to alternating electrical voltage. As the tip of the sonicator probe comes into contact with the liquid, mechanical vibration ensues, resulting in cavitations, which are the primary cause of ultrasonically generated effects. Cavitation refers to the creation and collapse of vapour cavities in a moving liquid. A vapour cavity arises when the local pressure drops to the temperature of the flowing liquid due to variations in local velocity. When these cavities collapse, intense shock waves propagate throughout the solution along the tip's radiating face, fracturing the distributed droplets.

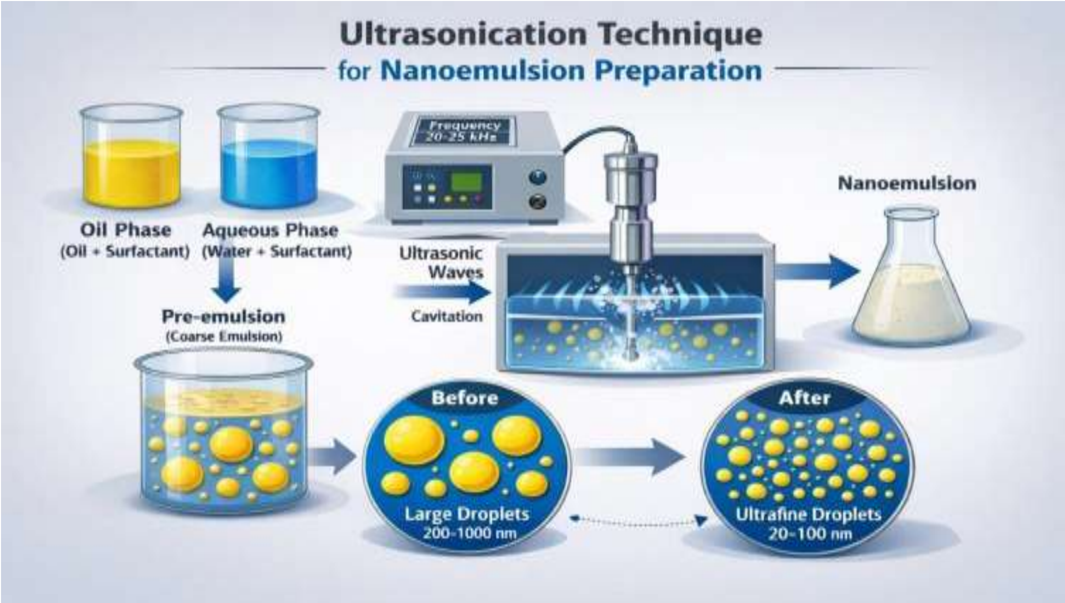

Fig 3 Ultrasonication Technique

Microfluidizer: [30]

Emulsion can be produced at even greater pressures up to about 700 Mpa. Two jets of crude emulsion from two opposing channels meet in the microfludizer nozzle, which is the central component of this apparatus (the interaction chamber). A pneumatically powered pump that can pressurise the in-house compressed air (150/650 Mpa) up to roughly 150 Mpa delivers the process stream.

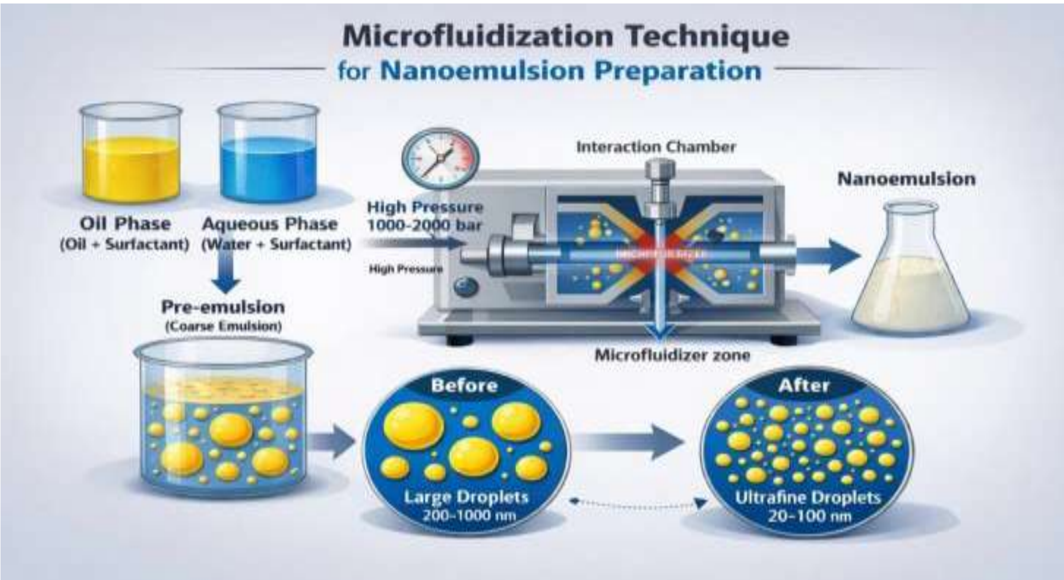

Fig 4 Microfluidization Technique

II. Low/Energy Emulsification Method [31]:

Low energy techniques can also be used to accomplish nano-emulsification, producing smaller, more homogeneous droplets. By utilising the physicochemical characteristics of the system, techniques like phase inversion temperature and phase inversion component produce smaller and more consistent droplets.

- **Spontaneous Nano-emulsification: [32]** During the emulsification process, it benefits from the chemical energy replacement based on the dilution process with the continuous phase, which typically takes place at a constant temperature without any phase transitions in the system. This technique doesn't require any extra equipment and can create nanoemulsions at ambient temperature.

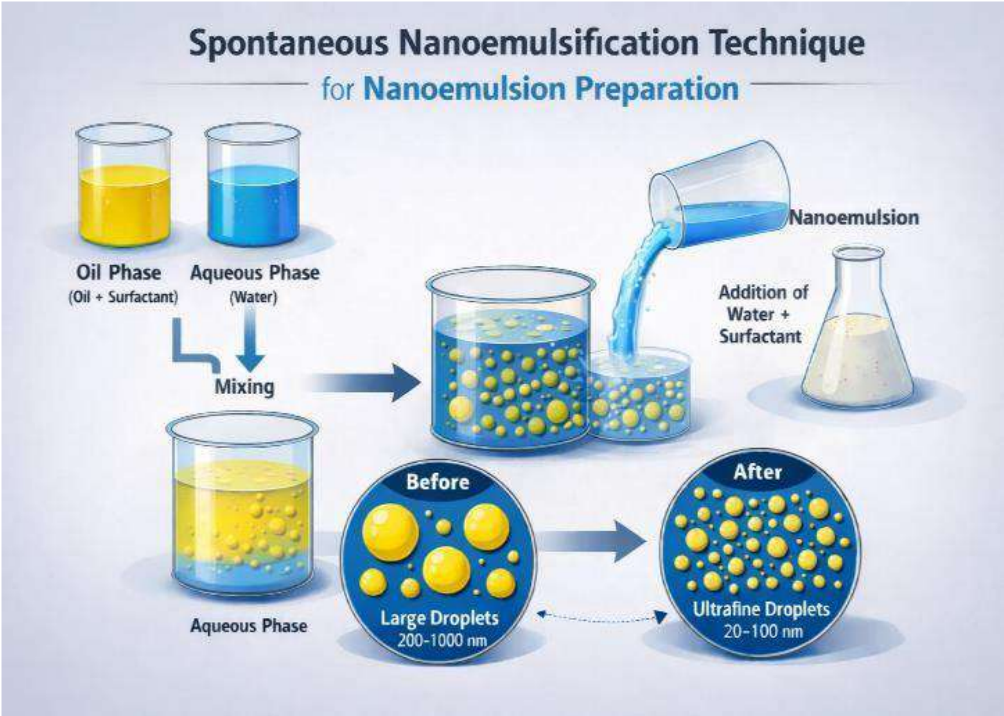

Fig 5 Spontaneous Nano-emulsification

Phase Inversion Temperature (PIT): [33] This technique modifies the temperature while maintaining a consistent composition. Polyethoxylated surfactants and other non-ionic surfactants with temperature-ependent solubility are crucial. By altering surfactant affinities for water and oil in response to temperature, emulsification is accomplished.

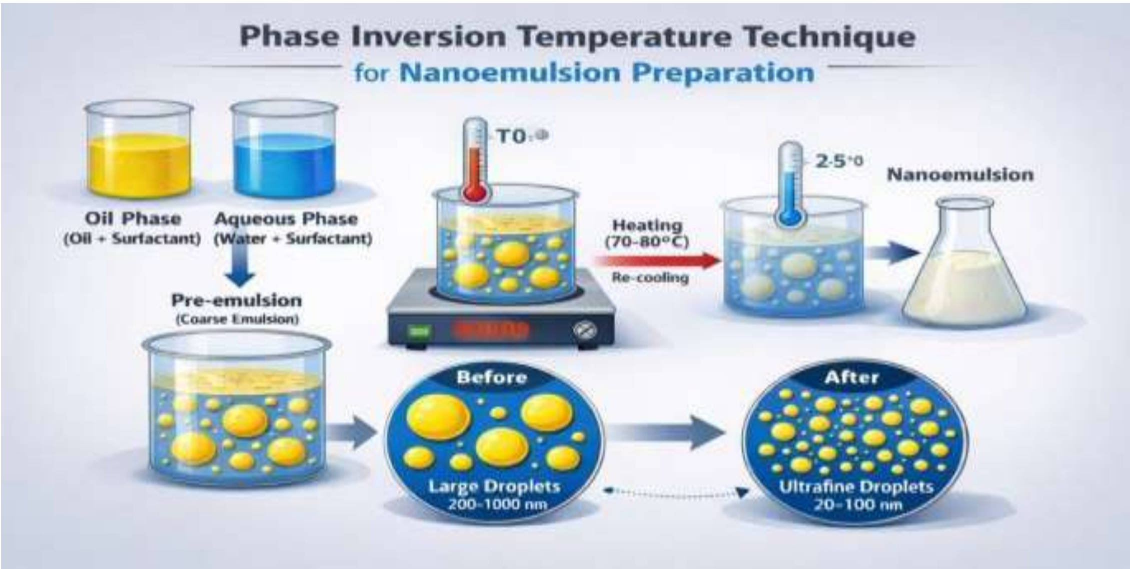

Fig 6 Phase Inversion Temperature

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- **Phase Inversion Composition (PIC): [34]**

This technique modifies composition while maintaining a steady temperature. Water or oil is continuously added to the oil-surfactant or water/surfactant mixture to create nanoemulsions. Since it is simpler to add one component to an emulsion than to produce an abrupt shift in temperature, the PIC approach is better suited for large-scale production than the PIT method.

Fig 7 Phase Inversion Composition

CHARACTERISATION
EVALUATION OF NANOEMULSION

Evaluation is essential to ensure the physicochemical stability, safety, photoprotective efficacy, and skin performance of nanoemulsion sunscreen compositions. The evaluation parameters that were often reported in the reviewed studies are summarised below.

1. **Droplet size and the Polydispersity Index (PDI) [35]**

Droplet size analysis is a critical component influencing the physical stability, skin penetration, transparency, and SPF efficacy of nanoemulsion sunscreens. In nanoemulsions, droplet diameters are typically smaller than 200 nm, ensuring uniform dispersion and enhanced photoprotection.

The Polydispersity Index (PDI) shows how regular the size distribution is. PDI values below 0.3 indicate a homogeneous nanoemulsion system. The technique is called Dynamic Light Scattering (DLS).

2. **The Zeta Potential [35]**

The zeta potential determines the electrostatic stability of nanoemulsions. Improved droplet repulsion, which prevents aggregation, is demonstrated by higher absolute values (±30 mV). Nanoemulsion sunscreens with a high enough zeta potential exhibit long-term physical stability.

3. **Determining pH [36]**

The pH of sunscreen formulations should be between 5.0 and 7.0 to avoid irritation. Nanoemulsion sunscreens often maintain a constant pH during storage.

4. **Studies on Viscosity and Rheology [37]**

Viscosity affects skin film-forming ability, consumer acceptability, and spreadability. Nanoemulsion sunscreens often exhibit Newtonian or pseudoplastic flow behaviour.The Brookfield viscometer method can be used to estimate this.

5. **Test for Spreadability [37]**

Spreadability reflects both uniform film generation and ease of application, both of which are necessary for effective UV protection. The parallel plate method can be used to test it by applying weight.

EVALUATION OF SUNSCREEN:

1. Sun Protection Factor (SPF) in Vitro [38]

SPF is the most important measure of UVB protection ability. Nanoemulsions often offer higher SPF because UV filters are better solubilised and more evenly distributed: UV spectrophotometric method based on the Mansur equation

2. Evaluation of UVA Protection [38]

UVA protection is evaluated using photobleaching methods or UVA/UVB ratios. Effective nanoemulsion sunscreens exhibit broad-spectrum protection. Methods: β-carotene bleaching assay Trans-resveratrol photobleaching method

3. Study of In-Vitro Drug Release [39]

This test evaluates the release behaviour of UV filters from nanoemulsion devices. Through regulated release, skin penetration is reduced and photostability is improved. Franz diffusion cell using a synthetic membrane technique

4. Studies on Skin Permeation and Deposition [39]

Research on skin penetration ensures that UV filters remain on the stratum corneum and do not penetrate the body.

5. Research on Photostability [40]

Photostability evaluates UV filters' resistance to degradation under UV radiation. Nanoemulsion methods improve photostability by encasing UV filters.

6. Research on Stability [40]

Stability studies assess the effects of different storage conditions on SPF, appearance, pH, and droplet size. At room temperature, elevated (40±2°C) and chilled (4 °C).

V. CONCLUSION

Sunscreen systems based on nanoemulsions have become a cutting-edge and successful method in contemporary photoprotection. The solubility, homogeneous dispersion, skin penetration, and overall sun protection factor (SPF) of sunscreen formulations are all greatly enhanced by the smaller droplet size of nanoemulsions. Numerous research have shown that nanoemulsion technology improves sunscreens' physicochemical characteristics and UV-protective effectiveness. When added to nanoemulsion systems, natural oils like avocado oil, bioactive antioxidants like spirulina and effluent from olive mills, and synthetic UV filters like bemotrizinol show increased efficacy. Additionally, compared to conventional emulsions, nanoemulsions offer better formulation stability, improved cosmetic acceptability, and a reduced risk of skin irritation.

The studied literature demonstrates a developing trend in sunscreen formulation towards the incorporation of nanotechnology, natural bioactives, and sustainable formulation methodologies. Lipid-based nanocarriers improve the stability, solubility, and encapsulation efficiency of organic UV filters, whilst herbal-based formulations provide safer, antioxidant-rich skin protection. Nanoemulsions boost SPF in a synergistic manner by enhancing the solubility, dispersion, and photostability of UV-absorbing chemicals.

Future research should concentrate on integrating these sophisticated methodologies, which include herbal antioxidants, lipid nanocarriers, and Pickering stabilisation techniques.Next-generation sunscreen formulations that provide improved photoprotective performance while reducing environmental impact and enhancing long-term safety could be created using such approach.

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