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Effect of Solvents on the *In Vitro* Sun Protection Factor and Broad-Spectrum Protection of Three Organic UV Filters

MARIAM ABOU-DAHECH, ALLISON SCHAEFER,
LAURA LAM-PHAURE, AN HUYNH, MARK CHANDLER, and
GABRIELLA BAKI, *Department of Pharmacy Practice, College of Pharmacy and Pharmaceutical Sciences, University of Toledo, Toledo, OH 43614 (M.A., A.S., L.L.-P., A.H.,G.B.), ACT Solutions Corp, Newark, DE 19713 (M.C.)*

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Synopsis

Solvents play an essential role in the performance of ultraviolet (UV) filters. The goal of this study was to understand how the *in vitro* sun protection factor (SPF) and broad-spectrum protection of three organic UV filters (homosalate, ethylhexyl salicylate, and butyl methoxydibenzoylmethane) and a combination of these are influenced by solvents. Twenty-four solvents were selected based on the ingredient active gap for testing. Mixtures of UV filters and solvents were formulated, and *in vitro* SPF, wavelength of maximum absorbance, broad-spectrum protection, and spreadability were evaluated. Results indicate that *in vitro* SPF of organic sunscreens can be significantly enhanced by solvents. Relying on solubility data only was not found to be a good approach in this study. The most efficient solvents shared multiple similar structural characteristics, including ester bonds, conjugated structure, aromatic rings, and –CN groups; however, the absence of some of these structural elements did not necessarily prevent a solvent from being a booster. The wavelength of maximum absorbance was significantly shifted in the UVA range by most solvents, whereas minimal or no shift was observed in the UVB range. Results of this study provide practical information that can guide sunscreen formulators in selecting solvents for UV filters and making more effective sunscreens.

INTRODUCTION

Ultraviolet (UV) radiation has a variety of biological and clinical effects on the skin ranging from erythema to pigmentation (1) to premature aging (2) and skin cancer. A common approach to prevent the damaging effects of UV radiation on the skin is to reduce intentional exposure to UV radiation and use sunscreens. Recent legislations in Hawaii

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Address all correspondence to Gabriella Baki at Gabriella.Baki@utoledo.edu.

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(3); Key West, FL (4); and the Virgin Islands (5) in the United States have banned two monographed organic UV filters, namely, oxybenzone [International Nomenclature of Cosmetic Ingredients (INCI) benzophenone-3] and octinoxate (INCI: ethylhexyl methoxycinnamate) because of their harmful environmental effects (6). The United States has a low number of UV filters to start with and the over-the-counter (OTC) monograph restricts certain combinations. Now, with the bans, sunscreen formulators in the United States have a very limited selection of organic UV filters they can incorporate into sunscreen products, and it is challenging to achieve a reasonably high SPF and broad-spectrum protection. The need for SPF and broad-spectrum protection boosting technologies is greater than ever.

For an organic UV filter to be an effective sunscreen, it must be soluble in at least a portion of the sunscreen formulation (7). Therefore, solvents play an essential role in the performance of sunscreens. Traditionally, octanol–water partition coefficient (logP) was used as an indication of lipophilicity and solubility. A newer approach is to use Hansen solubility parameters (HSPs), which are more versatile and look at solubility from a more complex approach (8). Each ingredient has three HSPs, δD for dispersion, δP for polarity, and δH for hydrogen bonding, which define its location in a three-dimensional space, the HSP space. HSP is based on the theory of "like dissolves like." Ingredients with similar HSPs dissolve well in each other, whereas dissimilar HSP values indicate that two ingredients will not mix/dissolve in each other. Formulating for Efficacy™ (FFE, ACT Solutions Corp., Newark, DE) is a computer program that matches active and inactive ingredients based on their HSPs (9). In addition to matching ingredients, FFE also calculates the ingredient active gap (IAG). IAG refers to the similarity of the ingredient and active ingredient (i.e., solvent and UV filter in this study). In general, the smaller the IAG, the more alike the active and solvent, and as "like dissolves like," the solubility will be higher. HSPs and IAG are applied in many sectors, including pharmaceuticals (10,11), personal care products (12), polymers (13–15), and paints and coatings (16,17). Using HSPs and IAG allows for a logical and streamlined selection process, which can save time and money for formulators.

Solvents often have different labels on supplier datasheets, including emollient, photostabilizer, and SPF booster. The current trend is to achieve a high SPF with only small amounts of UV filters because of economical, ecological, sensorial, and health-related reasons (7). A way to achieve this goal is to incorporate ingredients in the formulation that can attain better UV performance with less UV filters. Solvents have an important role in dissolving UV filters and contributing to the aesthetics of the product. In addition, certain emollients have been found to contain the properties of UV filters and, therefore, impart an SPF of their own (18). Solvent polarity was also found to affect the wavelength of maximum absorbance (λ_{max}) and critical wavelength in sunscreen formulations (19). In this project, our goal was to evaluate the effect of 24 solvents on the *in vitro* SPF, λ_{max}, and broad-spectrum protection (i.e., critical wavelength) of three organic UV filters and a blend of these three UV filters. Solvent selection was based on a modern approach, i.e., IAG calculated by FFE.

MATERIALS

UV filters included avobenzone [INCI: butyl methoxydibenzoylmethane (BMDM), United States Adopted Name (USAN): avobenzone] and homosalate (INCI/USAN: homosalate) purchased from Making Cosmetics (Redmond, WA), and Neo Heliopan OS® (INCI: ethylhexyl salicylate, USAN: octisalate) provided by Symrise (Elyria, OH). Today, the most widely used UVB filters in the United States include benzophenone-3, octocrylene, homosalate, and ethylhexyl salicylate (7). Because of the aforementioned bans, we only selected the "coral-safe" UVB filters to study. Butyl methoxydibenzoylmethane is one of the most efficient UVA-absorbing filters used around the globe, and it is the only UVA-absorbing organic filter approved in the United States. Because no single UV filter is capable of providing a high SPF and broad-spectrum protection, the combination of the three filters was tested as well.

Solvents selected by FFE included isododecane and cyclomethicone (INCI: cyclotetrasiloxane and cyclopentasiloxane) purchased from Making Cosmetics; SymMollient PDCC® (INCI: propanediol dicaprylate/caprate), Corapan TQ® (INCI: diethylhexyl 2,6-naphthalate), and Hydrolite 5® (INCI: pentylene glycol) provided by Symrise; Crodamol SFX® (INCI: PPG-3 benzyl ether ethylhexanoate), Cromollient ESP® (INCI: tris(PPG-3 benzyl ether) citrate), and super-refined castor oil provided by Croda (Mill Hall, PA); Kollicream IPM® (INCI: isopropyl myristate) and Myritol 318® (INCI: caprylic/capric triglyceride) provided by BASF (Florham Park, NJ); Eastman GEM® (INCI: 2-ethylhexyl palmitate) provided by Eastman (Miami, FL); AC Olive Oil Clear® [INCI: *Olea europaea* (olive) fruit oil] provided by Active Concepts (Lincolnton, NC); Finsolv TN® (INCI: C12-15 alkyl benzoate) provided by Innospec (Houston, TX); Lipex Shealight® (INCI: shea butter ethyl esters) provided by AAK (Karlshamn, Sweden); mineral oil (INCI: mineral oil) purchased from The Personal Formulator (Evanston, WY); sunflower seed oil [INCI: *Helianthus annuus* (sunflower) seed oil] purchased from Spectrum Chemical (New Brunswick, NJ); Schercemol 318® (INCI: isopropyl isostearate) provided by Lubrizol (Wickliffe, OH); LexFeel Natural® (INCI: heptyl undecylenate) provided by INOLEX (Philadelphia, PA); Hallbrite BHB® (INCI: butyloctyl salicylate), Hallstar DIPA® (INCI: diisopropyl adipate), SolaStay S1® (INCI: ethylhexyl methoxycrylene), and Polycrylene® (INCI: polyester-8) provided by Hallstar (Chicago, IL); Belsil DM 10® (INCI: dimethicone) provided by Wacker Chemie (Adrian, MI); and ethanol purchased from Decon Laboratories Inc. (King of Prussia, PA).

METHODOLOGY

FFE™

A search was made on UL Prospector for a list of emollients commonly used as solvents for UV filters. The keywords used in the search included "sunscreen solvent," "sunscreen solubilizer," "sunscreen photostabilizer," and "UV filter solvent." Boosters are usually defined as ingredients that can significantly increase the SPF without meaningfully contributing to SPF. Photostabilizers are molecules that can reduce or avoid the photodegradation of UV filters. Solvents are liquids used to dissolve ingredients in products, provide a vehicle for formulations, and also contribute to the texture of products. The same ingredient can often fulfill multiple functions. For example, photostabilizers often boost the overall SPF by preventing the UV filter from degradation, which makes them multifunctional ingredients. For simplicity purposes, we called all the ingredients screened and then selected for testing solvents.

The UL Prospector search resulted in 102 solvents. The solvents were entered into FFE using their canonical simplified molecular-input line-entry system (SMILES). Based on the SMILES, HSPs were generated and IAG was calculated. With FFE's own default solvents, a total of 167 solvents were ranked for each UV filter and the blend of UV filters based on the IAG. In addition, we evaluated the ingredient list of 12 commercial sunscreens to understand which solvents/potential SPF booster ingredients they included. FFE predications and findings from commercial products helped us select 24 solvents for this project (Table I).

UV FILTER–SOLVENT MIXTURES

Mixtures containing a ratio of 1:9 UV filter:solvent (w/w) were prepared for the *in vitro* SPF testing. One gram of UV filter was measured into a beaker on an analytical balance with a readability of 0.001 g, and 9 g of solvent was added to it. The beaker was placed on a magnetic stir plate and mixed at 650 rpm for 10 min for liquid UV filter–solvent mixtures. Solid UV filter–solvent mixtures were placed on a magnetic stirrer with hot plate at 85°C for 30 min at 650 rpm.

In addition, another set of mixtures was created containing the maximum allowed concentration of each UV filter (i.e., 15% of homosalate, 5% ethylhexyl salicylate, and 3% of butyl methoxydibenzoylmethane) per the OTC monograph (20). These mixtures contained

Table I
IAG between Each Solvent and UV Filter/UV Filter Blend Calculated by FFE™

	INCI name	IAG with H	IAG with EHS	IAG with BMDM	IAG with UV filter blend
1	Isododecane	9.78	10.0	**12.14**	10.08
2	Cyclotetrasiloxane and cyclopentasiloxane	**11.94**	**11.81**	**14.64**	**12.22**
3	*Olea europaea* (olive) fruit oil	*3.26*	*2.92*	7.97	*3.61*
4	C12-15 alkyl benzoate	*2.47*	3.04	4.63	2.65
5	Shea butter ethyl esters	5.00	5.25	7.75	5.32
6	Mineral oil	5.08	5.19	8.13	5.42
7	Helianthus annuus (sunflower) seed oil	2.98	2.69	6.64	3.33
8	Isopropyl isostearate	4.79	4.67	8.10	5.12
9	Dimethicone	**11.70**	**11.60**	**14.41**	**11.99**
10	Heptyl undecylenate	5.01	5.22	7.82	5.33
11	Isopropyl myristate	4.53	4.66	7.57	4.87
12	Caprylic/capric triglyceride	6.23	6.67	8.46	6.52
13	Ethanol	**15.49**	**14.53**	**17.54**	**15.48**
14	Ricinus communis (castor) oil	5.90	6.09	7.97	6.11
15	Propanediol dicaprylate/caprate	3.76	3.69	6.96	4.07
16	2-Ethylhexyl palmitate	5.97	6.25	8.55	6.28
17	Diethylhexyl 2,6-naphthalate	4.10	4.44	6.71	4.39
18	Pentylene glycol	**15.01**	**14.14**	**16.66**	**16.8**
19	PPG-3 benzyl ether ethylhexanoate	3.54	3.88	6.44	3.87
20	Tris(PPG-3 benzyl ether) citrate	3.16	2.77	6.81	3.49
21	Butyloctyl salicylate	1.46	1.54	4.98	1.79
22	Diisopropyl adipate	3.67	3.13	7.12	4.11
23	Ethylhexyl methoxycrylene	0.98	1.98	3.42	1.08
24	Polyester-8	3.17	3.49	5.68	3.41

H: homosalate, EHS: ethylhexyl salicylate, BMDM: butyl methoxydibenzoylmethane.
Values in italics denote excellent quality, in-bold denote poor quality, and those without formatting denote good quality.

2.3 g of UV filters and 7.7 g of solvent and were prepared using the aforementioned method. Each mixture was allowed to sit for 10 min after mixing to determine solubility. Signs of physical separation were visually determined.

IN VITRO SPF AND CRITICAL WAVELENGTH TESTING AND WAVELENGTH OF MAXIMUM ABSORBANCE

The Food and Drug Administration (FDA) 2011 method (21) was used for testing *in vitro* SPF (Labsphere UV-2000S, North Sutton, NH) using polymethylmethacrylate (PMMA) plates (HelioScreen HelioPlates HD6, Labsphere). A 5 × 5-cm PMMA plate was tared on an analytical balance with a readability of 0.001 g. As per the FDA method, 2 mg/cm^2 of the UV filter–solvent mixture (total of 50 mg) was applied to the plate, and using a finger cot, the mixture was spread in a circular motion for 30 s, vertical motion for 15 s, and horizontal motion for another 15 s to ensure complete and even coverage. Then the plate was placed in a dark drawer for 15 min. Each plate was scanned in five different locations, each UV filter–solvent mixture was tested on three different plates. The software (UVS2000 Application, Labsphere) measured absorbance and converted it to *in vitro* SPF using an algorithm.

In the United States, to label a sunscreen broad spectrum, the product has to have a critical wavelength of at least 370 nm. Critical wavelength is the wavelength below which 90% of the area under the absorbance curve resides (21). The same PMMA plates and same amount of UV filter–solvent mixture was used for broad-spectrum testing. Critical wavelength was calculated by the Labsphere software. The λ_{max} values were obtained from the absorbance results.

SPREADABILITY TESTING

Spreadability of each solvent was determined using a TA.XT*Plus* texture analyzer (Texture Technologies Corp., Hamilton, MA) and a spreadability fixture. Test mode was set to “measure force in compression,” and “return to start” option was used. Trigger type was set to “button.” The male cone’s penetration distance was set to 1 mm less than the starting point distance. Test speed and post-test speed were set to 3.0 mm/s. Exponent stable micro-systems software (version 6.1.10.0, Texture Technologies Corp., Hamilton, MA) was used to generate spreadability curves.

STATISTICAL ANALYSIS

Differences in *in vitro* SPF, λ_{max}, critical wavelength, and spreadability were evaluated using one-way analysis of variance followed by Tukey’s multiple comparison test using SPSS Statistics 21 software (IBM, Armonk, NY). A p value less than 0.05 was taken as the minimal degree of statistical significance.

RESULTS

FFE

FFE calculated the IAG for each UV filter–solvent mixture (Table I). Among the solvents tested, there were excellent solvents (arbitrary IAG range: 1–5), good solvents (arbitrary

IAG range: 6–10), and poor solvents (arbitrary IAG range: >10) for each UV filter. IAG ranged from 0 to 39 when looking at all 167 solvents in FFE; for good solvency, the number should be as low as possible. In the case of homosalate, ethylhexyl salicylate, and the UV filter blend, most solvents (i.e., 16 of 24) were excellent based on FFE predictions. As for butyl methoxydibenzoylmethane, most solvents (i.e., 16 of 24) were considered good.

Four solvents were ranked poor for all UV filters and the UV filter blend: two silicones, including dimethicone and a blend of cyclotetrasiloxane and cyclopentasiloxane; ethanol, a semipolar solvent; and pentylene glycol, a polar solvent. Next in line was isododecane, which was ranked good for the UVB filters and the UV filter blend and poor for butyl methoxydibenzoylmethane.

Butyl methoxydibenzoylmethane did not dissolve in any of the solvents ranked poor and five good solvents (i.e., 5 of 16). We did not observe a trend in the IAG number and ability of a good solvent to dissolve butyl methoxydibenzoylmethane. Some good solvents had higher numbers and worked, e.g., caprylic/capric triglyceride, whereas others did not work, although they had a lower number, e.g., *Helianthus annuus* (sunflower) seed oil. Three solvents were ranked excellent for all UV filters and the UV filter blend, including C12-15 alkyl benzoate, butyloctyl salicylate, and ethylhexyl methoxycrylene.

IN VITRO SPF AND CRITICAL WAVELENGTH TESTING AND WAVELENGTH OF MAXIMUM ABSORBANCE

Most solvents tested had *in vitro* SPF values close to 1 (Table II). Four solvents had *in vitro* SPF values above 2, including butyloctyl salicylate (SPF 19.5), diethylhexyl 2,6-naphthalate (SPF 35.2), polyester-8 (SPF 50.3), and ethylhexyl methoxycrylene (SPF 330.2). The *in vitro* SPF of homosalate alone was 13.7 ± 2.8, and ethylhexyl salicylate 12.7 ± 1.9. Measuring the *in vitro* SPF of butyl methoxydibenzoylmethane alone was not possible because of its waxy nature. Butyl methoxydibenzoylmethane has to be dissolved to provide sun protection. Solvents change their absorbance spectra; therefore, calculating the SPF of butyl methoxydibenzoylmethane from any of the mixtures was not possible either. Measuring the *in vitro* SPF of each UVB filter alone helped understand the extent of SPF boost. Testing was not performed for mixtures in which avobenzone was insoluble; this is indicated in the tables.

A theoretical *in vitro* SPF was calculated for each UVB filter–solvent mixture by adding 10% of the UV filter's SPF to 90% of the solvent's SPF. Any measured number higher than the theoretical number was considered a boost. In any 1:9 mixture, homosalate was assumed to have an *in vitro* SPF of 1.4 and ethylhexyl salicylate 1.3. The theoretical SPF of the blend could not be calculated because of butyl methoxydibenzoylmethane's unknown theoretical SPF.

All UVB filter–solvent mixtures—except for the isododecane mixture—had a higher *in vitro* SPF than the sum of the SPF of the UV filter and solvent would yield, indicating a synergistic and not just additive relationship. The four solvents with a high inherent SPF (diethylhexyl 2,6-naphthalate, butyloctyl salicylate, ethylhexyl methoxycrylene, and polyester-8) did not boost the SPF of the individual UVB filters. The SPF of these mixtures was significantly higher ($p < 0.05$) in most cases than the rest of the mixtures, but the high SPF was a result of the solvents' inherent SPF and not a synergism between the UV filter and solvent.

Table II

Solvents Used and Mixtures Created in This Study and Their In Vitro SPF (Values Are Displayed as Average and SD)

	INCI name	Ingredient alone	1:9 Mixture with H	1:9 Mixture with EHS	1:9 Mixture with BMDM	2.3:7.7 Mixture with UV filter blend
1	Homosalate	13.7 ± 2.8	N/A	N/A	N/A	N/A
2	Ethylhexyl salicylate	12.7 ± 1.9	N/A	N/A	N/A	N/A
3	Isododecane	1.0 ± 0.1	2.4 ± 0.1	2.8 ± 0.4	-	-
4	Cyclotetrasiloxane and cyclopentasiloxane	1.0 ± 0.1	4.4 ± 0.4	4.7 ± 0.2	-	-
5	Olea europaea (olive) fruit oil	1.0 ± 0.1	6.0 ± 2.0	6.7 ± 1.2	14.8 ± 5.2	22.1 ± 4.5
6	C12-15 alkyl benzoate	2.0 ± 0.2	6.0 ± 0.6	6.9 ± 0.9	15.4 ± 2.1	14.8 ± 1.8
7	Shea butter ethyl esters	1.5 ± 0.3	5.0 ± 0.6	6.9 ± 1.4	25.7 ± 5.5	18.5 ± 2.4
8	Mineral oil	1.0 ± 0.1	6.9 ± 0.7	6.7 ± 2.8	-	-
9	Helianthus annuus (sunflower) seed oil	1.0 ± 0.1	6.4 ± 0.6	7.9 ± 0.7	-	-
10	Isopropyl isostearate	1.0 ± 0.1	5.5 ± 0.7	5.1 ± 0.8	-	-
11	Dimethicone	1.0 ± 0.1	5.6 ± 0.1	6.1 ± 0.2	-	-
12	Heptyl undecylenate	1.0 ± 0.1	6.5 ± 1.2	6.2 ± 1.0	14.9 ± 2.9	24.1 ± 4.8
13	Isopropyl myristate	1.0 ± 0.1	6.7 ± 1.3	5.6 ± 0.7	41.3 ± 1.6	14.4 ± 0.5
14	Caprylic/capric triglyceride	1.0 ± 0.1	6.4 ± 0.6	5.7 ± 0.6	10.9 ± 2.3	14.5 ± 3.0
15	Ethanol	1.0 ± 0.1	6.1 ± 0.6	7.4 ± 0.5	-	-
16	Ricinus communis (castor) oil	1.0 ± 0.1	7.7 ± 1.7	7.0 ± 1.4	-	-
17	Propanediol dicaprylate/caprate	1.0 ± 0.1	6.8 ± 1.8	7.2 ± 0.4	11.7 ± 1.2	15.5 ± 3.8
18	2-Ethylhexyl palmitate	1.0 ± 0.1	6.1 ± 1.0	5.8 ± 1.5	-	-
19	Diethylhexyl 2,6-naphthalate	35.2 ± 5.4	28.9 ± 1.8	26.0 ± 11.8	37.3 ± 1.9	30.9 ± 2.1
20	Pentylene glycol	1.0 ± 0.1	5.4 ± 0.6	4.3 ± 0.2	-	-
21	PPG-3 benzyl ether ethylhexanoate	1.0 ± 0.1	6.0 ± 1.3	7.0 ± 0.6	32.2 ± 2.5	14.9 ± 2.8
22	Tris(PPG-3 benzyl ether) citrate	1.1 ± 0.1	8.4 ± 1.2	7.7 ± 0.7	23.3 ± 4.5	26.2 ± 3.0
23	Butyloctyl salicylate	19.5 ± 1.6	13.7 ± 5.3	9.3 ± 2.5	70.1 ± 3.4	18.0 ± 1.4
24	Diisopropyl adipate	1.0 ± 0.1	5.9 ± 1.0	5.9 ± 0.2	23.8 ± 4.5	19.0 ± 3.6
25	Ethylhexyl methoxycrylene	330.2 ± 74.9	397.2 ± 109.9	398.6 ± 101.3	225.5 ± 95.3	138.7 ± 20.6
26	Polyester-8	50.3 ± 1.9	90.5 ± 15.2	103.1 ± 22.0	466.2 ± 124.9	200.1 ± 88.7

H: homosalate, EHS: ethylhexyl salicylate, BMDM: butyl methoxydibenzoylmethane. - refers to solvents in which BMDM was insoluble.

The four solvents that had the highest SPF alone shared common structural characteristics, including ester bonds, conjugated structure, and aromatic ring(s). Aromatic rings and a conjugated structure potentially allowed for many possible resonance structures to exist when excited with an electron. Stronger absorption at longer wavelengths equates to a higher SPF value. Aromatic rings have an utmost importance for the UV spectroscopic properties of molecules. Nothing proves its importance more than the fact that today all organic UV filters have aromatic moieties (22). In addition, ethylhexyl methoxycrylene and polyester-8 also had cyano (–CN) groups in their conjugated structure. CN groups have two pi (π) bonds, which allow for more electron delocalization compared with a double bond that has just one π bond. When counting the total number of π bonds present in each molecule, polyester-8 has 22, ethylhexyl methoxycrylene has 10, diethylhexyl 2,6-naphthalate has seven, and tris(PPG-3 benzyl ether) citrate has 12. However, it is also important to understand that the most stable molecules have their π bonds in a conjugated structure. Thus, although tris(PPG-3 benzyl ether) citrate has 12 π bonds overall, only three are positioned in a conjugated manner. In comparison, diethylhexyl 2,6-naphthalate only has seven π bonds overall; however, all are in a conjugated structure together. This is why diethylhexyl 2,6-naphthalate had a higher SPF in every case. When looking at ethylhexyl methoxycrylene, it has all of its 10 π bonds in a conjugated structure, which explains its higher SPF.

Although these structural characteristics are important, their presence did not guarantee a solvent to have a high SPF alone. For example, C12-15 alkyl benzoate, PPG-3 benzyl ether ethylhexanoate, and tris(PPG-3 benzyl ether) citrate had aromatic rings and conjugated structure; however, their *in vitro* SPF alone was around 1. Some solvents, such as *Olea europaea* (olive) oil, shea butter ethyl esters, heptyl undecylenate, and diisopropyl adipate contained ester bonds but did not possess aromatic moieties or a conjugated structure. The *in vitro* SPF of these solvents was also around 1. They all significantly boosted the SPF when combined with UV filters (<0.05), especially tris(PPG-3 benzyl ether) citrate, which achieved one of the highest SPF values for the UV filter blend, but they did not have a high SPF themselves.

In addition to strictly looking at the chemical structure, the mechanism of action of the solvents also has to be considered. Some solvents tested in this study are sold as photostabilizers. When chemical UV filters absorb light, the energy from the UV photons convert them from the ground state to the excited state. After the energy is dissipated, electrons will return to the ground state, and the UV filter is ready to receive the next UV photon. Some UV filters, such as butyl methoxydibenzoylmethane, are photounstable, and their chemical structure changes in the excited state, which prevents them from absorbing the next UV photon. Photostabilizers are molecules that are able to reduce or avoid the photodegradation of UV filters. A common approach to photostabilization is to quench the excited state (either singlet or triplet state) of the UV filter and quickly return the UV filter to the ground state (23,24). Examples for this mechanism include triplet-state quenchers diethylhexyl 2,6-naphthalate and polyester-8 and singlet-state quencher ethylhexyl methoxycrylene. For a photostabilizer to be effective, it has to show a similar energy level to that of the photoexcited state of the photounstable molecule to absorb the excitation energy (7). This is the reason why photostabilizers are often also UV absorbers (25), as we also observed this phenomenon in this work. The photostabilizing mechanism of action of butyloctyl salicylate is different from the aforementioned solvents. Butyloctyl salicylate has a high dielectric constant, making it highly polar. Matching the polarity of the solvent to that of the UV filter(s) has been shown to reduce UV filter degradation (26).

The *in vitro* SPF of the homosalate–solvent mixtures ranged from 2.4 to 397.2 (Table II). The four highest SPFs were provided by diethylhexyl 2,6-naphthalate, butyloctyl salicylate, ethylhexyl methoxycrylene, and polyester-8. The same four solvents resulted in the highest SPF for ethylhexyl salicylate as well; in this case, the SPF ranged from 2.8 to 398.6. The butyl methoxydibenzoylmethane–solvent mixtures had higher SPF values than the UVB filter–solvent mixtures, except for ethylhexyl methoxycrylene. The *in vitro* SPF values ranged from 10.9 to 466.2 in this case. The *in vitro* SPF of the UV filter blend–solvent mixtures was higher in every case than the SPF of the individual UVB filter–solvent mixtures but lower than the butyl methoxydibenzoylmethane–solvent mixtures in many cases. The SPF ranged from 14.4 to 200.1. In the case of the UV filter blend–solvent mixtures, ethylhexyl methoxycrylene, polyester-8, diethylhexyl 2,6-naphthalate, and tris(PPG-3 benzyl ether) citrate resulted in the highest SPF values.

Based on all the aforementioned observations, it can be concluded that structural elements, including ester bonds, conjugated structure, aromatic rings, and –CN groups are important, but are not the only characteristics that can influence the SPF and SPF-boosting capability of a solvent. The photostabilizing effect of the solvents and polarity have also been shown to influence the λ_{max} and molar absorptivity (19) of UV filters.

Most solvents transmitted almost all light in the UV region, which is in correlation with the *in vitro* SPF results. Exceptions were C12-15 alkyl benzoate, diethylhexyl 2,6-naphthalate, butyloctyl salicylate, ethylhexyl methoxycrylene, and polyester-8, which absorbed light in both the UVB and UVA regions (Figure 1A). Ethylhexyl methoxycrylene barely had any transmittance in the UV region. Most mixtures of the UVB filters homosalate and ethylhexyl salicylate covered efficiently UVB and some of UVA-II but transmitted practically 100% of the radiation in the UVA-I region (Figures 1B and C). Exceptions were the mixtures with diethylhexyl 2,6-naphthalate, ethylhexyl methoxycrylene, and polyester-8, which absorbed light even in the UVA-I region. It was noted that isododecane and a blend of cyclotetrasiloxane and cyclopentasiloxane when combined with ethylhexyl salicylate transmitted about 60% in the UVA range until 360 nm. Butyl methoxydibenzoylmethane transmitted about 5–10% in the UVB region and less than 5% in the UVA region (Figure 1D). This was an unusual finding considering that the literature classifies butyl methoxydibenzoylmethane as a UVA filter; therefore, no UVB protection was expected from it (7,27,28). The potential of butyl methoxydibenzoylmethane to absorb light in the UVB region is briefly mentioned in one source (7). The UV filter blend was very similar to butyl methoxydibenzoylmethane, it transmitted about 5–10% in the UVB region and less than 10% in the UVA region (Figure 1E).

We also determined which mixtures would pass the critical wavelength test. The UVB filters were not expected to pass the test; however, in the case of both homosalate and ethylhexyl salicylate, the mixtures with ethylhexyl methoxycrylene had a critical wavelength >370 nm (387 and 386 nm, respectively; Table III). The inherent UV-absorbing capacity was responsible for this unexpected result. Ethylhexyl methoxycrylene had a broad-spectrum protection as it can be seen in Figure 1. In the case of butyl methoxydibenzoylmethane, all mixtures had a critical wavelength >370 nm, as it was expected given that butyl methoxydibenzoylmethane is a UVA filter. For the UV filter blend–solvent mixture, all mixtures had a critical wavelength >370 nm.

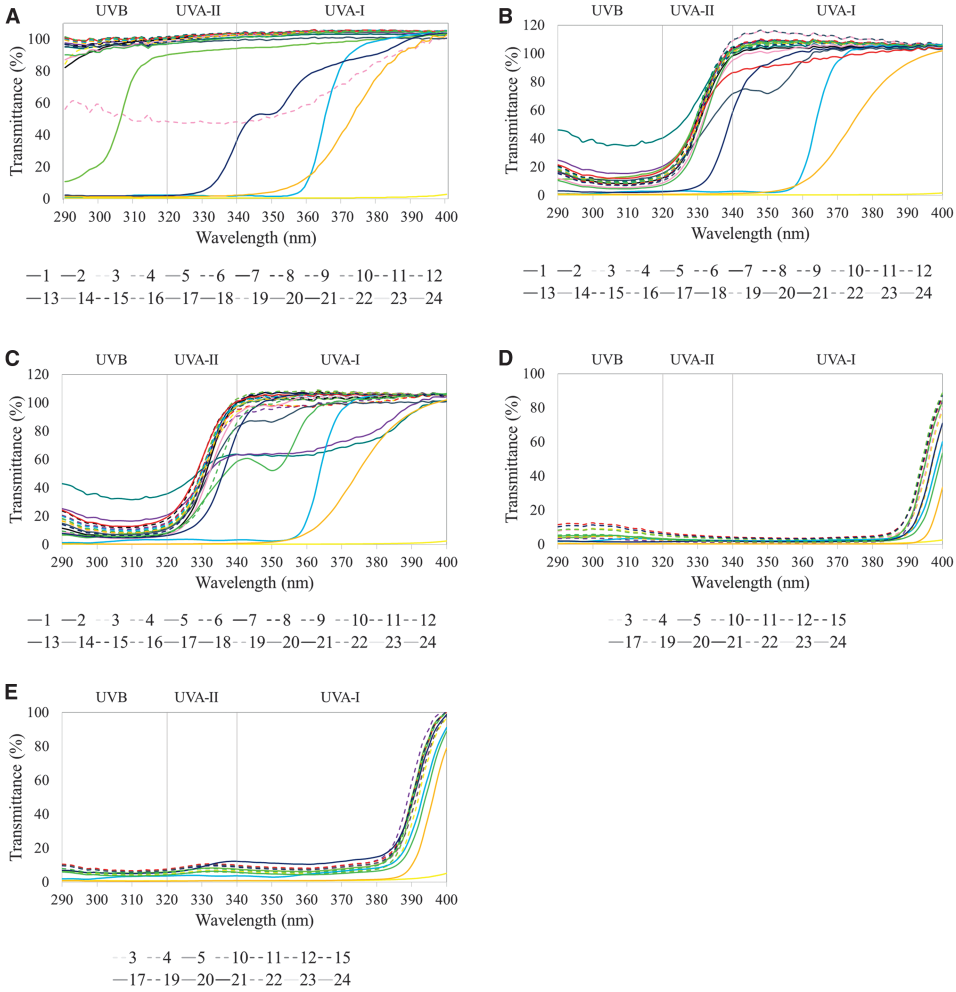

Figure 1. Transmittance spectra. (A) Solvents alone. (B) Homosalate–solvent mixtures. (C) Ethylhexyl salicylate–solvent mixtures. (D) Butyl methoxydibenzoylmethane–solvent mixtures. (E) UV filter blend–solvent mixtures.

Potential shift in the λ_{max} was also studied. Having a shift in λ_{max} could affect UV filter's efficacy and ability to provide optimal protection to the skin against UV rays. An ingredient may be a good booster or photostabilizer, but if it negatively affects the efficacy of a UV filter, it is not recommended to be used. The λ_{max} for homosalate and ethylhexyl salicylate was at 311 nm, and for butyl methoxydibenzoylmethane at 357 nm (29). The UV filter blend was expected to have two peaks, one correlating with the UVB filters, and the other with the UVA filter. Three solvents, including butyloctyl salicylate, ethylhexyl methoxycrylene, and polyester-8 had an absorption peak at 311, 312, and 311 nm, respectively. This finding is in correlation with the aforementioned results, referring to the inherent UV-absorbing capacity of the solvents. Diethylhexyl 2,6-naphthalate had three main peaks: the highest at 297 nm, the second highest at 350 nm, and the third at 335 nm.

Two solvents shifted the λ_{max} of homosalate significantly ($p < 0.05$) toward shorter wavelengths (hypsochromic shift), including shea butter ethyl esters and diethylhexyl

Table III
Critical Wavelength (nm) of the UV Filter–Solvent Mixtures

	INCI name	1:9 Mixture with H	1:9 Mixture with EHS	1:9 Mixture with BMDM	2.3:7.7 Mixture with UV filter blend
1	Isododecane	324	357	-	-
2	Cyclotetrasiloxane and cyclopentasiloxane	322	354	-	-
3	Olea europaea (olive) fruit oil	323	326	382	378
4	C12-15 alkyl benzoate	321	325	382	378
5	Shea butter ethyl esters	322	323	381	377
6	Mineral oil	323	324		
7	Helianthus annuus (sunflower) seed oil	324	323	-	-
8	Isopropyl isostearate	322	322	-	-
9	Dimethicone	322	323	-	-
10	Heptyl undecylenate	323	322	381	377
11	Isopropyl myristate	322	328	380	376
12	Caprylic/capric triglyceride	322	326	381	377
13	Ethanol	331	330	-	-
14	Ricinus communis (castor) oil	325	321	-	-
15	Propanediol dicaprylate/caprate	323	323	381	377
16	2-Ethylhexyl palmitate	322	323	-	-
17	Diethylhexyl 2,6-naphthalate	353	353	383	377
18	Pentylene glycol	327	319	-	-
19	PPG-3 benzyl ether ethylhexanoate	323	324	383	378
20	Tris(PPG-3 benzyl ether) citrate	323	328	384	380
21	Butyloctyl salicylate	330	329	382	377
22	Diisopropyl adipate	322	320	381	377
23	Ethylhexyl methoxycrylene	387	386	387	386
24	Polyester-8	356	356	384	379

H: homosalate, EHS: ethylhexyl salicylate, BMDM: butyl methoxydibenzoylmethane. - refers to solvents in which BMDM was insoluble.

2,6-naphthalate (Table IV and Figure 2B). The rest of the solvents only caused a minimal shift (1–2 nm) toward either the shorter or longer wavelengths. In the case of ethylhexyl salicylate, shea butter ethyl esters, diethylhexyl 2,6-naphthalate, and tris(PPG-3 benzyl ether) citrate shifted the λ_{max} significantly toward shorter wavelengths ($p < 0.05$, Table IV and Figure 2C), the rest of the solvents did not cause a significant change. The mixtures of diethylhexyl 2,6-naphthalate and the UVB filters had three absorption peaks, similar to diethylhexyl 2,6-naphthalate alone. All solvents except for diisopropyl adipate caused a significant shift in butyl methoxydibenzoylmethane's λ_{max} ($p < 0.05$); diethylhexyl 2,6-naphthalate shifted the λ_{max} toward a shorter wavelength, whereas the rest of the solvents caused a bathochromic shift. Diethylhexyl 2,6-naphthalate, butyloctyl salicylate, and polyester-8 caused double peaks for butyl methoxydibenzoylmethane (Table IV and Figure 2D). In the case of the UV filter blend, diethylhexyl 2,6-naphthalate caused a significant hypsochromic shift ($p < 0.05$); the rest of the solvents did not cause a significant change in the UVB region (Table IV and Figure 2E). Isopropyl myristate, ethylhexyl methoxycrylene, and polyester-8 did not cause a significant change in the UVA range, whereas the rest of the solvents shifted the λ_{max} ($p < 0.05$) to either a shorter wavelength (diethylhexyl 2,6-naphthalate) or longer wavelength (rest of the solvents).

Table IV
Wavelength of Maximum Absorbance

		Homosalate	Ethylhexyl salicylate	Butyl methoxy-dibenzoylmethane	Mixture
	INCI name	Wavelength (nm)			
1	Isododecane	310	310	-	-
2	Cyclotetrasiloxane and cyclopentasiloxane	309	310	-	-
3	Olea europaea (olive) fruit oil	309	310	361	310, 361
4	C12-15 alkyl benzoate	310	310	361	310, 361
5	Shea butter ethyl esters	297	297	362	310, 361
6	Mineral oil	310	310	-	-
7	Helianthus annuus (sunflower) seed oil	309	310	-	-
8	Isopropyl isostearate	309	309	-	-
9	Dimethicone	309	309	-	-
10	Heptyl undecylenate	309	309	361	310, 361
11	Isopropyl myristate	309	309	361	310, 359
12	Caprylic/capric triglyceride	309	309	361	310, 361
13	Ethanol	309	309	-	-
14	Ricinus communis (castor) oil	309	310	-	-
15	Propanediol dicaprylate/caprate	309	309	361	310, 361
16	2-Ethylhexyl palmitate	309	310	-	-
17	Diethylhexyl 2,6-naphthalate	297 (and 335, 351)	297 (and 335, 350)	297 (and 350)	297 (and 335, 350)
18	Pentylene glycol	309	309	-	-
19	PPG-3 benzyl ether ethylhexanoate	309	309	361	310, 361
20	Tris(PPG-3 benzyl ether) citrate	309	297	362	310, 361
21	Butyloctyl salicylate	310	310	311, 362	310, 361
22	Diisopropyl adipate	309	309	358	310, 360
23	Ethylhexyl methoxycrylene	312	311	362	311, 355
24	Polyester-8	311	312	311, 361	311, 358

- refers to solvents in which BMDM was insoluble.

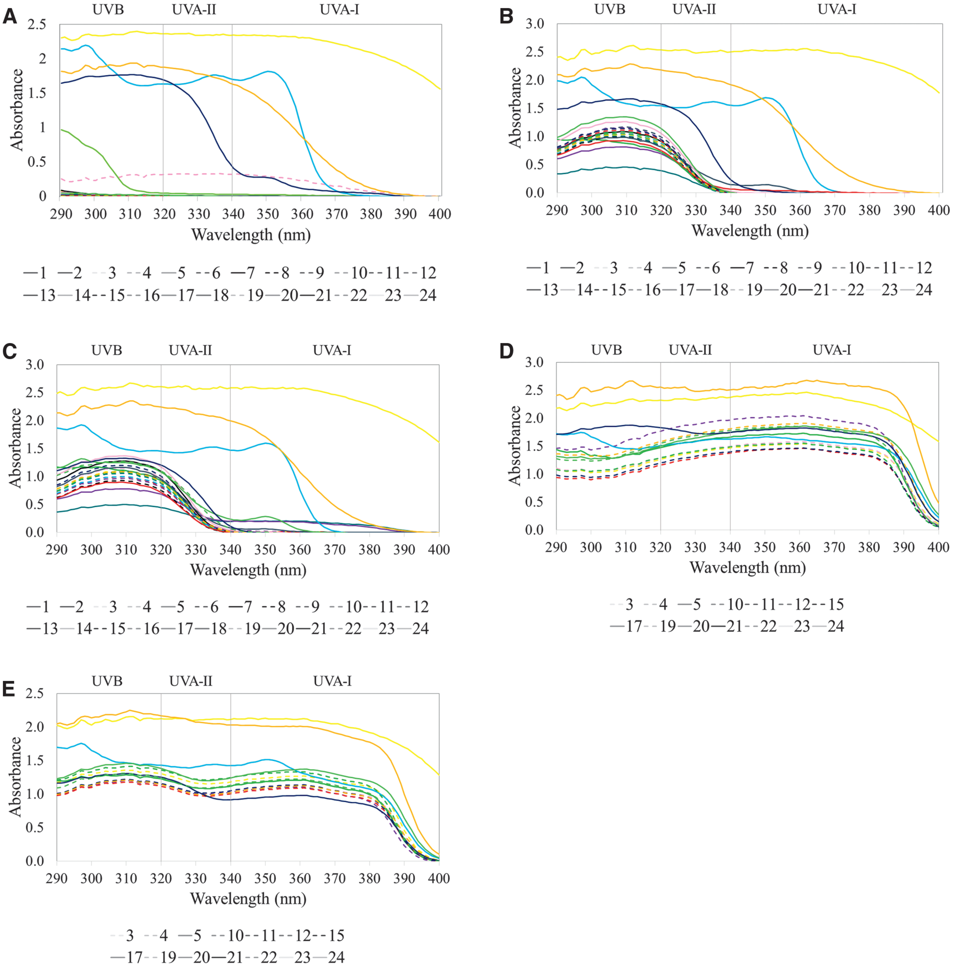

Figure 2. Absorption spectra. (A) Solvents alone. (B) Homosalate–solvent mixtures. (C) Ethylhexyl salicylate–solvent mixtures. (D) Butyl methoxydibenzoylmethane–solvent mixtures. (E) UV filter blend–solvent mixtures.

Overall, it can be concluded that we did not observe a direct relationship between the chemical structure and IAG value of a solvent and the ability to cause a shift in the λ_{max}.

SPREADABILITY

Sunscreens are often deemed greasy by consumers, which could lead to lower compliance (30). Emollients have been shown to contribute to the afterfeel of emulsions (21,31). We tested the spreadability of each solvent (most of which were emollients) to understand their potential effect on the skin feel of products. It should be noted that the goal of this project was not to create realistic sunscreens, we analyzed mixtures of solvents and UV filters to understand how solvents may change the *in vitro* SPF and broad-spectrum absorbing properties of the UV filters. Formulators typically combine multiple solvents to achieve a desired product performance and skin feel. Analyzing spreadability can help formulators make a decision about how much of a solvent should be used to boost the SPF, but at the same time, not to have a negative impact on the skin feel of the product.

The positive peak is a measure of firmness. Because we worked with liquid ingredients, the firmness values were considerably low in most instances. Firmness of skin cream gels is typically in the range of 120–200 g (32), and skin creams could have even higher values (33). Two solvents had relatively higher numbers, still under 100 g, including mineral oil and *Helianthus annuus* (sunflower) seed oil (Table V). Only a few solvents had numbers above 200 g, including *Ricinus communis* (castor) oil, diethylhexyl 2,6-naphthalate, tris(PPG-3 benzyl ether) citrate, ethylhexyl methoxycrylene, and polyester-8, with the last two being above 3,000 g. The area under the positive curve is the measure of energy required to deform a sample to the defined distance. Firmness and positive area together indicate the spreadability of a sample. A higher firmness and more hardness work carried out indicate a less spreadable sample, whereas a lower positive peak and smaller area under the curve indicate a more spreadable sample. Firmness and overall spreadability values correlated well with each other. Ethylhexyl methoxycrylene and polyester-8 had by far the highest numbers, referring to their extremely poor spreading nature. The two most spreadable solvents were isododecane and ethanol. The negative peak indicates adhesive forces within the sample. The seven solvents that were considered firmer and less spreadable had the highest numbers for stickiness as well, with ethylhexyl methoxycrylene and polyester-8 being extremely sticky. The negative area under the curve gives an indication of adhesiveness of a solvent. A sticky sample is typically described as a more cohesive. Cream gels typically have a negative peak in the range of 80–150 g (32), creams may have even higher values (33). Similar to the positive area under the curve, the negative area under the curve correlated well with the negative peak. The stickiest and most cohesive solvents were ethylhexyl methoxycrylene and polyester-8.

Overall, many solvents that boosted the SPF had poor spreadability and a sticky nature, including diethylhexyl 2,6-naphthalate, ethylhexyl methoxycrylene, and polyester-8. Using a higher amount of these solvents in a sunscreen could have a negative effect on the skin feel. In addition, ethylhexyl methoxycrylene and polyester-8 have a distinct color (yellow and amber, respectively), which could affect the color of the finished product when used in a larger amount. Butyloctyl salicylate on the other hand proved to be a relatively good SPF booster in this study without having a sticky and low spreading nature.

CONCLUSIONS

Twenty-four solvents commonly used in sunscreens and/or advertised by suppliers as sunscreen solvents, emollients for UV filters, photostabilizers, and/or SPF boosters were evaluated for their ability to boost the *in vitro* SPF of two UVB filters and a UVA filter and a combination of these three filters. Critical wavelength, potential shift in λ_{max}, and spreadability were also analyzed.

In this project, we used IAG to determine solubility. IAG indicated that most solvents would perform excellently with the UVB filters and UV filter blend, whereas they would only be good for butyl methoxydibenzoylmethane in most cases. Relying on IAG data only was not found to be a good approach in this study. Solvents, which achieved the highest *in vitro* SPF when mixed with UV filters (butyloctyl salicylate, diethylhexyl 2,6-naphthalate, ethylhexyl methoxycrylene, and polyester-8) shared multiple similar

Table V
Spreadability of Each Solvent

	INCI name	Peak positive (firmness)	Positive area (hardness work done)	Peak negative (stickiness)	Negative area (adhesiveness)
		g	g.sec	g	g.sec
1	Isododecane	8.5 ± 0.3	0.1 ± 0.0	−10.5 ± 0.5	−0.0 ± 0.1
2	Cyclotetrasiloxane and cyclopentasiloxane	9.1 ± 0.1	7.7 ± 0.2	−9.7 ± 0.1	−0.0 ± 0.0
3	Olea europaea (olive) fruit oil	11.8 ± 0.2	8.4 ± 0.2	−9.4 ± 0.6	−0.1 ± 0.0
4	C12-15 alkyl benzoate	15.0 ± 0.1	9.0 ± 0.2	−11.2 ± 0.0	−1.3 ± 0.0
5	Shea butter ethyl esters	10.6 ± 0.1	7.7 ± 0.3	−9.4 ± 0.2	−0.1 ± 0.0
6	Mineral oil	62.1 ± 0.7	20.1 ± 0.1	−55.6 ± 0.8	−8.1 ± 0.1
7	Helianthus annuus (sunflower) seed oil	46.1 ± 0.2	15.8 ± 0.5	−37.7 ± 0.3	−5.1 ± 0.0
8	Isopropyl isostearate	12.3 ± 0.1	8.3 ± 0.2	−10.6 ± 0.4	−0.1 ± 0.0
9	Dimethicone	10.4 ± 0.4	7.3 ± 0.6	−9.9 ± 0.3	−0.1 ± 0.0
10	Heptyl undecylenate	9.2 ± 0.1	7.2 ± 0.1	−9.0 ± 0.3	4.7 ± 3.4
11	Isopropyl myristate	9.7 ± 0.1	7.2 ± 0.5	−10.4 ± 0.8	−0.1 ± 0.0
12	Caprylic/capric triglyceride	21.4 ± 0.1	10.3 ± 0.4	−15.1 ± 0.1	−1.9 ± 0.0
13	Ethanol	8.9 ± 0.1	0.1 ± 0.0	−9.3 ± 0.3	−0.0 ± 0.0
14	Ricinus communis (castor) oil	477.5 ± 4.8	107.5 ± 1.5	−484.1 ± 3.2	−57.6 ± 0.4
15	Propanediol dicaprylate/caprate	13.5 ± 0.1	8.9 ± 0.3	−10.7 ± 0.1	−0.1 ± 0.0
16	2-Ethylhexyl palmitate	13.6 ± 0.1	8.3 ± 0.1	−11.2 ± 0.3	−1.1 ± 0.0
17	Diethylhexyl 2,6-naphthalate	238.0 ± 3.6	62.7 ± 0.5	−224.8 ± 18.2	−30.5 ± 0.5
18	Pentylene glycol	27.3 ± 0.1	11.8 ± 0.1	−21.4 ± 0.1	−2.7 ± 0.1
19	PPG-3 benzyl ether ethylhexanoate	16.0 ± 0.1	9.3 ± 0.7	−11.5 ± 0.0	−1.2 ± 0.0
20	Tris(PPG-3 benzyl ether) citrate	278.0 ± 6.3	71.9 ± 0.9	−277.1 ± 6.4	−35.6 ± 1.1
21	Butyloctyl salicylate	17.3 ± 0.2	10.0 ± 0.4	−12.3 ± 0.2	−1.5 ± 0.0
22	Diisopropyl adipate	10.0 ± 0.1	8.3 ± 0.3	−9.5 ± 0.2	−0.1 ± 0.0
23	Ethylhexyl methoxycrylene	3,837.4 ± 35.8	1,273.8 ± 12.5	−3,765.4 ± 42.8	−768.5 ± 13.7
24	Polyester-8	3,252.8 ± 37.5	1,040.5 ± 14.7	−3,238.9 ± 43.4	−640.0 ± 15.3

structural elements, including ester bonds, conjugated structure, and aromatic ring(s). Ethylhexyl methoxycrylene and polyester-8 also had –CN groups. These four solvents had an inherent SPF-absorbing capacity as well, which led to the high SPF of the UV filter–solvent mixtures. Our results indicated that these structural characteristics are important and can indicate good performance; however, the absence of some of these structural elements did not necessarily prevent a solvent from being a booster. Multiple solvents caused a significant hypsochromic or bathochromic shift in the UV filters' λ_{max}, especially for butyl methoxydibenzoylmethane. However, in all cases, the λ_{max} stayed in the range where the UV filter was normally absorbed in. In the case of the UVB filters, most solvents only caused a minimal or no shift. Although polyester-8 and ethylhexyl methoxycrylene achieved the highest SPF values, they were viscous and sticky and had a strong color. Optimizing their use level is recommended to achieve good performance and acceptable aesthetics.

For a formulator to select and estimate the effect of a solvent on the UV-absorbing characteristics of a UV filter, solubility of the UV filter in the solvent, chemical structure, and mechanism of action of the solvent and solvent–UV filter interactions should be considered. Results of this study provide practical information that can guide sunscreen formulators in selecting solvents for UV filters and making more effective sunscreens.

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