综述评论

Research on Sucrose Esters—Natural Glycosyl Surfactants: A Review

WANG Kui

WANG Kui, JIANG Jian-chun*, GAO Yi-wei, LI Xiang-yu

(Institute of Chemical Industry of Forestry Products, CAF; National Engineering Lab. for Biomass Chemical Utilization; Key of Open Lab. on Forest Chemical Engineering, SFA; Key Lab. of Biomass Energy and Material, Jiangsu Province, Nanjing 210042, China)

Abstract: This paper aims at presenting a review of the available literatures on the preparation technology of natural nonionic glycosyl surfactant sucrose esters(SE), such as acyl chloride esterification method, transesterification method and enzyme-catalysis method. It is pointed out that transesterification method is a mature technology which includes solvent method, water solvent method and solvent-free method. According to different methods, this review also describes the purification and detection presents the problem in the most convenient way and discusses the potential future research areas.

Key words: glycosyl; natural surfactants; sucrose esters

CLC numbers: TQ35; TQ423 **Document code**: A **Article ID**: 0253 - 2417(2011)06 - 0100 - 07

糖基天然表面活性剂蔗糖酯的研究综述

王 奎, 蒋剑春, 高一苇, 李翔宇

(中国林业科学研究院 林产化学工业研究所; 生物质化学利用国家工程实验室; 国家林业局 林产化学工程重点开放性实验室; 江苏省生物质能源与材料重点实验室, 江苏 南京 210042)

摘 要: 综述了非离子糖基天然表面活性剂蔗糖酯的各种合成方法: 酰氯酯化法、酯交换法、酶催化法等。重点介绍了现有的较成熟的酯交换法的各种工艺, 包括溶剂法, 水溶剂法和无溶剂法, 并介绍了不同合成方法相应的精制工艺和检测方法, 指出了现有各种工艺的优点和缺陷, 并展望了我国蔗糖酯工业发展的趋势。

关键词: 糖基; 天然表面活性剂; 蔗糖酯

All liquids, under certain conditions, have surface tension. At normal temperature, the surface tension of water is 72.75 mN/m, benzene is 28.88 mN/m and hexane is 18.43 mN/m. Surfactant is the material that can significantly reduce the surface tension of solvent and interfacial tension of liquid/liquid, and is known as 'industrial monosodium glutamate'[1]. In 1996, the world demand of surfactants besides soap was approximately 9×10^6 t, the total demand reached 10.8×10^6 t in 2000, 13×10^6 t in 2005, and 15×10^6 t in 2010[2].

According to the structure of hydrophilic groups, the surfactants can be classified to cationic surfactants, anionic surfactants, amphoteric surfactants, nonionic surfactants, bio-surfactants and other special types of surfactants[3]. As a kind of glycosyl natural nonionic surfactant, sucrose ester(SE) has the advantages of wide variety of sources, naturally renewable, biodegradable, non-toxic to the nature and human body, which is

收稿日期: 2011 - 03 - 28
基金项目: 国家 863 计划资助 (2010AA1016020); 国家自然科学基金资助项目(30700634)
作者简介: 王 奎(1985 -), 男, 江苏徐州人, 博士生, 研究方向为生物质能源与生物基材料; **E-mail**: way910@163.com
* **通讯作者**: 蒋剑春, 研究员, 博士, 博士生导师, 研究领域为林产化学加工和生物质能源开发技术; **E-mail**: bio-energy@163.com。

different from other kind of surfactants. A number of polar hydroxyl end groups determine the SE with more hydrophilic, oil repellency and better chemical properties in the oil-water system and more development room and market prospects[4-6]. Sucrose esters have been deeply researched and widely used in food, pharmaceutical, cosmetic and material industries[7-17]. However, due to the development of the market, special sucrose esters of high monoesters content and high purity are demanded for the fine application, which can hardly be obtained by the existing processes.

This paper aims to present a review of the available literatures on the preparation, purification and detection of SE, present the advantage and problems of most available findings and discuss the potential future research areas.

1 Preparation of SE

The synthesis of sucrose esters can be traced back to the 19th century. Sucrose esters were synthesized by esterification of sucrose and fatty acids or anhydride, or chloride acylation of sucrose and fatty acyl chloride in pyridine solution. The process is carried out in a solvent, which has high toxicity, low yield and high cost. The process is, therefore, undesirably complicated for use on an industrial scale. A high-yield transesterification process, showed by Osipow in 1956, used dimethylformamide as solvent. Although this process has a high yield, the solvent of high boiling point with high toxicity can still hardly be removed from products. The industrial device with an annual output of 300 t sucrose esters was established by Nippon Sugar Manufactured Kabushiki Kaisha in 1959, which marked a beginning of sucrose ester industrial production. In 1967, the continuous industrial production of sucrose esters with solvent method was implemented by Mitsubishi Formation Kabushiki Kaisha, the annual output was 1 200 t. In order to solve the problems which arise when using an organic solvent, a micro-emulsion process was developed by Osipow, using propanediol as the solvent. Based on it, Nippon First Pharmacy Kabushiki Kaisha improved the industrial production of sucrose esters in 1971, which used water as solvent. In 1975, a 3 000 t/a solvent-free industrial device was established by Mitsubishi Formation Kabushiki Kaisha. Following with the research on the synthesis and application of sucrose esters, phase transfer catalysis method, enzyme-catalysis method and other methods are adopted in the synthesis of sucrose ester which has high monoester content.

According to the reaction mode, the method of synthesis of sucrose esters can be classified into three types: acyl chloride esterification method, transesterification method and enzyme-catalysis method.

1.1 Acyl chloride esterification method

Chortyk et al[18] showed that, in the presence of nitro-organic compounds, such as quinoline, pyridine and other azine, esterification was conducted between sucrose and fatty acid chloride with pyridine as acid binding agent. The synthesized sucrose ester had high monoester content and yield. As using nitro-organic compounds as solvent and acid binding agent, the toxic solvent can be hardly removed from products. The products quality can not reach the industry standard of food, drug and cosmetic, which limit the application of sucrose esters.

1.2 Transesterification method

Based on the reaction mode, the method of transesterification can be categorized into three types: solvent method, water solvent method and solvent-free method.

1.2.1 Solvent method　Solvent method is the earliest transesterification method, using dimethylformamide or dimethylsulfoxide as solvent, sucrose ester is prepared by transesterification between sucrose and short-chain fatty acid ester in the presence of catalyst.

Yukio et al[19] showed that, using water and methanol as solvent, sucrose, potassium hydroxide and

potassium soap were stirred at 55-60 ℃, the residue was dried for 4 h to obtain an adduct in the form of fine powder. And then sucrose stearate of high substitution was added, the mixture was allowed to react at 100 ℃ and 133.3 kPa for 3 h. The yield of sucrose esters was 76.9 %, and the average degree of substitution of the SE was 2.5.

William et al[20] displayed that, transesterification was conducted between sucrose and ethyl stearate in the presence of potassium carbonate, the mixture was dissolved in dimethylsulfoxide and stirred at 95 ℃ for 4 h, the purity of refined sucrose esters was 92 %.

Although the solvent method has high quality of product and high conversion of sucrose and oil, it still has disadvantage arising from the use of toxic solvent which can not be easily removed from the product.

1.2.2 Water-solvent method Water-solvent method is an improved process on micro-emulsion method by Kogyo Seiyaku Co. Ltd.[21], and was industrially produced in 1971. Sucrose and potassium stearate were added in water to form a sucrose-soap solvent, a substantial portion of the added water was removed at an elevated temperature of the solution between 100-125 ℃, and potassium carbonate was then introduced into the system, thereafter, methyl ester of beef tallow fatty acid was added while remaining water was being gradually removed at an elevated temperature of 150 ℃ under a reduced pressure of 8.0 kPa for 3 h to thereby obtain the product. It was found that 95 % of the added methyl ester of beef tallow fatty acid was converted to sucrose ester and the content of monoester was 62 %.

Although this process avoids the problems which arise when using an organic solvent, it is a multi-stage process which still requires heating under reduced pressure, and the pressure must be carefully controlled in relation to the temperature when producing the dehydrated melting, in order to avoid hydrolysis of the fatty acid ester.

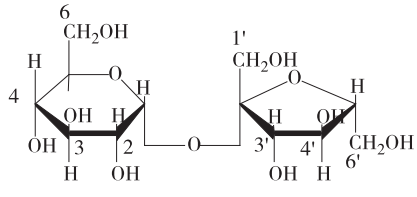
1.2.3 Solvent-free method Solvent-free method is the most extensively applied process in preparing sucrose esters at present, transesterification is conducted in the absence of a solvent.

A new process was disclosed by Juliette and Yves[22]. Solid particulated sucrose, triglyceride, potassium carbonate powder, potassium tallowate and tallow were mixed in the absence of any solvent. Then, the mixture was stirred at 125℃ under an atmosphere of dry nitrogen for 4 h and the samples was analyzed by gas liquid chromatography. The purity of sucrose esters was 80.2 % and the monoester content was 39.4%.

A solvent-free process in the presence of phase transfer catalyst was showed by Urata et al[23]. Using potassium carbonate as a base initiator and didodecyldimethyl ammonium bromide as a phase transfer catalyst, sucrose and cottonseed fatty acid methyl esters were combined and stirred at 110 ℃ under an atmosphere of N_2 for 2 h. The yield of sucrose octaester was 69% and the unreacted methyl ester content was 19%.

As a large different polarity between sucrose and fatty acid esters, fatty acid soap was added to solvent-free system as emulsifier in order to form an uniform emulsion system, or the phase transfer catalyst was added to promote the reaction. However the soap and the phase transfer catalyst can not be easily removed from the system. Thus, although solvent-free process avoids the problem arising from the use of solvent, it has disadvantages of its own tending to make it unsatisfactory as a commercial-scale sucrose ester surfactant.

1.3 Enzyme-catalysis method



Sucrose has three active primary alcoholic hydroxyls and five secondary alcoholic hydroxyls. The reaction activities of free hydroxyl groups follow the order OH-6 > OH-6′ > OH-1′ > secondary-OH. Great deals of isomers are easily obtained in the synthesis of sucrose esters, which limit the application of products. However, enzyme-catalysis method has good selectivity in the presence of dimethylformamide, dimethylsulfoxide or pyridine as solvent, or

in the absence of any solvent. According to the species of enzyme, enzyme-catalysis method can be classified into protease catalysis and lipase catalysis.

1.3.1 Protease catalyzed method Subtilisin protease has been used in regioselective synthesis of 1′-O-sucrose esters, which is hold as the only protease having activity in the presence of dimethylformamide. Ferrer and Cruces[24-25] showed that, using subtilisin as catalyst, 1′-O-butyrate sucrose was obtained by the transesterification between 2,2,2-trichloroethyl butyrate and sucrose in the presence of dimethylformamide, the yield of product was 57%. A new protease was used by Ninfa et al[26], which was called Protease N(Amano). Transesterification was conducted between $CH_3(CH_2)_nCO_2CH_2CF_3$ and sucrose in the presence of dimethylformamide. It was found that the yield of sucrose esters decreased with the increase of chain length, and the highest yield was 64 % when n equals 2. Pierre et al[27-28] showed that, using a new protease N(Fluka) as catalyst, transesterification was generated by vinyl methacrylate and sucrose in the presence of dimethylformamide, the yield was 93 %.

Using protease as catalyst in enzymatic synthesis of sucrose esters, the process can obtain high yield of 1′-O- sucrose esters. However, the selectivity was enhanced towards 1′-O- sucrose esters, and it is only suitable for the low chain of fatty acid esters. Furthermore the large toxicity of solvent limited the application of protease.

1.3.2 Lipase catalyzed methods A chemo-enzymatic synthesis of 6′-O- acylsucroses which included two steps was showed by Maja et al[29]. First, in the presence of 1,4-diazabicyclo-[2,2,2]octane as a catalyst, transesterification occurred between 3-acyl-5-methyl-1,3,4-thiadiazole-2-thiones and sucrose, 6′-O- acylsucroses and 6, 6′-O- acylsucroses were obtained. Then, 6,6′-O- acylsucroses was selectively and catalytically hydrolyzed and high purity of 6′-O- acylsucroses was obtained. Sinthuwat et al[30] showed that, as lipase has low activity in proton-inert solvent, sucrose was firstly acetalizated, then, esterification was conducted between sucrose acetal and long-chain fatty acid in the absence of any solvent and 6′-O-acylsucrose acetal was produced. 6′-O-Acylsucroses was obtained by the de-protection of 6′-O-acylsucrose acetal.

Lipase catalysis process expand the application of enzyme and avoid the limit of chain length of fatty acid. However, it is a multi-stage process which requires acetalization and de-protection, being unsatisfactory as a commercial-scale process for sucrose esters.

2 Purification of SE

All sucrose esters which are synthesized either in solvent, micro-emulsion, water, under solvent-free condition, or by enzyme catalysis, contain sucrose ester, unreacted sucrose, fatty acid, fatty acid soap, fatty acid ester, catalyst and other leftover. Due to the existence of impurity, it is necessary to refine the sucrose esters to match the demand of the areas of food, pharmaceutical and cosmetic. The refining technology influences the yield and quality of the product, and decides the price and application areas simultaneously.

2.1 Purification method in solvent process

The crude product, in solvent method process, contains sucrose esters, solvent, unreacted sucrose, catalyst and other impurities.

A research by Mohamed[31] showed that, the reaction products, which contained unreacted sucrose, soap and other residues, were dissolved in an equal quantity of warm butanone and the soap was acidified with lactic acid. The unreacted sucrose and excess of lactic acid were then eliminated by two extractions with distilled water. The solvent was then removed under reduced pressure to obtain the final sucrose esters. The purity of refined sucrose esters was 88.6 %.

A liquid-liquid extraction using a hardly water-miscible organic solvent was displayed by Yasuaki

et al[32], which is selected from an alcohol having at least 4 carbon atoms and a ketone having at least 4 carbon atoms. The process comprised: 1) the crude product was added into water and organic solvent, and the pH value of the aqueous phase was allowed to reduce below 7, to thereby extract dimethylsulfoxide into the aqueous phase, and the sucrose esters into an organic solvent phase; 2) the arising process was allowed to repeat by adding water to the organic solvent phase, to thereby extract dimethylsulfoxide remaining in the organic solvent solution into the aqueous phase; 3) sucrose ester was recovered from the organic solvent solution.

2.2 Purification method in non-solvent process

Based on the purification process of SE arising, a refining process can be conclude that: according to the fatty acid having an average carbon chain length of 16 or greater, ethyl alcohol or methyl ethyl ketone was added to break the system of the ester product and unreacted fatty acid ester. For fatty acid having an average carbon length of less than 16, adding ethyl alcohol or methyl ethyl ketone can not break the system. Two phase extraction, with water and an hardly water-miscible organic solvent, should be introduced to recover the sucrose esters and unreacted fatty acid ester. The organic solvent was an alcohol or a ketone having at least 4 carbon atoms. After the arising extraction process, ethyl acetate was used to wash the unreacted fatty acid ester away and the product quality may meet the standard of FDA.

It was noted that the preparation of SE was different due to the reaction system under specific conditions. The various processes in the preparation of SE can be categorized as solvent and nonsolvent processes. The solvent processes contain acyl chloride esterification method, enzyme-catalysis method and transesterification method in a solvent such as dimethylformamide, water, or propanediol. As using water, an organic solvent or solvent/water, the solvent processes usually obtain high content of monoester. However, certain quantities of solvent remaining in the product, which cannot be removed easily, limit the application of SE. Although the nonsolvent process avoids the disadvantages arising from the use of a solvent, it is a complex process which needs to be controlled exactly and usually obtains a low-purity product and low content of monoester. The purity and monoester content of SE by various methods were shown in Table 1.

Table 1 Purity and monoester content of SE by various methods %

solvent	solvent			non-solvent[1)]	
	solvent[18] DMSO	water[21] water	enzyme-cat.[28] DMF	soap[22] non	ptc[23] non
purity(after refining)	85.6	85	93	80.2	79
monoester content	70.5	62	93	39.4	69

1) ptc: phase transfer catalyst

With the development of pharmaceutical, cosmetic, material and food industry, the market demand for the sucrose ester with antibacterial, anti-oxidation, acidproof and other specific properties and special structure has being greatly increased. The SE produced by the past technologies was mainly composed of by monoester, diester, polyester, and the products contained a considerable amount of soap and other impurities. The product quality was difficult to meet the market demand. Therefore, the appropriate selection of oil material and synthesis technology, as well as the refining process designed to obtain high product quality and SE with special performance and structure will be the research emphasis.

3 Detection of SE

As sucrose has three active primary hydroxyls and five active secondary hydroxyls, the sucrose esters product usually contains sucrose monoester, sucrose diester, sucrose triester, fatty acid, unreacted sucrose and other residues. The detection of sucrose esters, thereby, was important for the determination of reaction endpoint, tracking purification process and confirming product quality. According to the detection mode, it

can be divided into chemical detection and instrumental detection.

3.1 Chemical detection

A standard for sucrose esters as food additive was introduced in GB 8272 – 2009[33] (Nation Standard of PRC). 25 mL ethanol solution of potassium hydroxide is added into a 250 mL conical flask which is charged with 1 g sample. Reflux condensation tube is equipped and the device is placed in water bath which can be heated. After heating till slight boiling for 1 h, the device is removed and allowed to cool, and then, 50 mL water is added, the mixture was concentrated to 30 and 10 mL hydrochloric acid solution is then introduced into the system, and sodium chloride was added while conical flask is shaking. The solution is removed to a separating funnel, and then, 30 mL ether and the system was allowed to be layered to two phases. The ether phase, after washing with 20 mL sodium chloride saturated solution, is dehydrated with 2 g anhydrous sodium sulfate. Then it is placed on hot water bath and dried in fume hood to obtain a white soft wafer. The water phase of 2 mL is introduced into a tube and heated on water bath in order to remove the remaining ether, the system was allowed to cool, and then, 1 mL anthrone-sulfuric acid is added along the tube wall. If the color of the solution turns to blue-green, the sample is confirmed to be sucrose esters.

3.2 Instrumental detection

TLC and GC-MS were used to detect the sucrose esters in the past decades. As sucrose esters did not display itself, and derivative process is needed while sucrose ester is detected by GC-MS. High performance liquid chromatography(HPLC) and HPLC with differential refractometer were introduced to detect the sucrose esters in recent years[34-35]. However the ultraviolet absorption of sucrose esters is weak and differential refractometer cannot be used in gradient elution. As evaporative light scattering can be used in gradient elution, HPLC with evaporative light scattering detection (ELSD) was considered to be the ideal detection of sucrose esters[36-37].

4 Conclusions

This study has been carried out to summarize and review the basic concepts, latest research methods and tools for understanding the preparation, purification and detection of SE. The various processes, advantages, and disadvantages, together with the possible areas of applications of different methods for preparation, purification and detection of SE have been discussed and described. It was concluded that the SE is mainly used as a glycosyl natural surfactant. The preparation of SE, which covers different methods under various conditions, are complex and important. More research and efforts are needed for achieving synthesizing special SE with high purity and high content of monoester. It was also concluded that there is a need to develop methods for purifying and detecting the SE used in pharmaceutical, cosmetic, material and food industries.

References:

[1] JULIAN E. Surfactant Chemistry[M]. Wuhan: Wuhan University Press, 2005.

[2] HOLMBERG K. Natural surfactants[J]. Current Opinion in Colloid & Interface Science, 2001, 6(2): 148-159.

[3] YVES Q, STÉPHANE C, CÉLINE B, et al. Recent progress in the synthesis of carbohydrate-based amphiphilic material. The examples of sucrose and isomaltulose[J]. Carbohydrate Research, 2008, 343(12): 1999-2009.

[4] IRENE J A B. Sugar fatty acid ester surfactants: Structure and ultimate aerobic bio-degradability[J]. Journal of Surfactants and Detergents, 2000, 3: 1-11.

[5] 李延科. 糖基表面活性剂蔗糖酯[D]. 大连: 大连理工大学博士学位论文, 2004: 1-149.

[6] CARLOS R, DURGA P A, SHIGEKI H, et al. Effect of ionic surfactants on the phase behavior and structure of sucrose ester/water/oil systems [J]. Journal of Colloid and Interface Science, 2003, 262(2): 500-505.

[7] CHANSANROJ K, BETZ G. Sucrose esters with various hydrophilic-lipophilic properties. Novel controlled release agents for oral drug delivery matrix tablets prepared by direct compaction[J]. Acta Biomaterialia, 2010, 6(8): 3101-3109.

[8] SAMIA S, STÉPHANIE O, JEAN M E, et al. Comparative study of some surface active properties of fructose esters and commercial sucrose esters

[J]. Colloids and Surfaces A:Physicochemical and Engineering Aspects,2003,227(1):35-44.
[9]KEVIN W S,ASAKO Y,MOTOMATSU A,et al. Decontamination of fresh produce by the use of slightly acidic hypochlorous water following pretreatment with sucrose fatty acid ester under microbubble generation[J]. Food Control,2010,21(9):1240-1244.
[10]TAKASHI K,YOSHIKAZU T,KATSUMI N. Adsorption of sorbitan fatty acid esters and a sucrose mono-alkanoate at the nitrobenzene-water interface and its effect on the rate of ion transfer across the interface[J]. Electrochimica Acta,1995,40(18):2869-2874.
[11]FANUN M,LESER M,ASERIN A,et al. Sucrose ester microemulsions as microreactors for model Maillard reaction[J]. Colloids and Surfaces A:Physicochemical and Engineering Aspects,2001,194(1):175-187.
[12]TUAL A,BOURLES E,BAREY P,et al. Effect of surfactant sucrose ester on physical properties of dairy whipped emulsions in relation to those of O/W interfacial layers[J]. Journal of Colloid and Interface Science,2006,295(2):495-503.
[13]GARTI N,ASERIN A,FANUN M. Non-ionic sucrose esters microemulsions for food applications[J]. Colloids and Surfaces A:Physicochemical and Engineering Aspects,2000,164(1):27-38.
[14]DELGADILLO J C,NAIK A,KALIA Y N,et al. Skin permeation enhancement by sucrose esters:A pH-dependent phenomenon[J]. International Journal of Pharmaceutics,2005,297,(1):204-212.
[15]LUUK A,HILGERS T,ANNEKE G B. Sucrose fatty acid sulphate esters as novel vaccine adjuvant[J]. Vaccine,2006,24(2):81-82.
[16]BARROS M T,PETROVA K T,SINGH R P. Synthesis and biodegradation studies of new copolymers based on sucrose derivatives and styrene [J]. European Polymer Journal,2010,46(5):1151-1157.
[17]MIDORI Y,SHINICHI K,DAI N,et al. Lack of toxicity or carcinogenicity of S-170,a sucrose fatty acid ester,in F344 rats[J]. Food and Chemical Toxicology,2004,42(4):667-676.
[18]CHORTYK O T,POMONIS J G,JOHNSON A W. Synthesis and characterization of insecticidal sucrose esters[J]. J Agric Food Chem,1996,44(6):1551-1557.
[19]YUKIO K,TETSURO Y. Process for preparing sucrose fatty acid esters:US,5527903[P]. 1996-07-18.
[20]WILLIAM A F,ROBERT W S. Sugar-ester manufacturing process:US,5756716[P]. 1998-05-26.
[21]FUMIAKI Y,YOSHIO K. Process for synthesizing sucrose esters of fatty acid:US,3792041[P]. 1974-04-12.
[22]JULIETTE F,YVES Q,JEAN P M,et al. Co-melting of solid sucrose and multivalent cation soaps for solvent-free synthesis of sucrose esters [J]. Tetrahedron Letters,2007,48(23):4111-4114.
[23]URATA K,TAKAISHI N. Application of phase transfer catalytic reactions to fatty acids and their derivatives. Present state and future potential [J]. J Am Oil Chem Soc,1996,73(7):831-839.
[24]FERRER M,CRUCES M A,PLOU F J,et al. Chemical versus enzymatic catalysis for the regioselective synthesis of sucrose esters of fatty acids [J]. Studies in Surface Science and Catalysis,2000,130:509-514.
[25]FERRER M,JUAN S,PLOU F J P,et al. Synthesis of sugar esters in solvent mixtures by lipases from *Thermomyces lanuginosus* and *Candida antarctica* B,and their antimicrobial properties[J]. Enzyme and Microbial Technology,2005,36(4):391-398.
[26]NINFA R P,REINHARD W,RUNE M,et al. Synthesis of sucrose laurate using a new alkaline protease[J]. Tetrahedron:Asymmetry,2003,14(6):667-673.
[27]PIERRE P,ALAIN B,JULIETTE G,et al. Proteinase N-catalysed regioselective esterification of sucrose and other mono- and disaccharides [J]. Tetrahedron:Asymmetry,2001,12(17):2409-2419.
[28]PIERRE P,ALAIN B,GÉRARD D,et al. Proteinase N-catalysed transesterifications in DMSO-water and DMF-water. Preparation of sucrose mono-methacrylate[J]. Tetrahedron Letters,2000,41(19):3597-3600.
[29]MAJA H,SASA S,ZELJKO K. Enzymatic synthesis of sugar fatty acid esters in organic solvent and in supercritical carbon dioxide and their antimicrobial activity[J]. The Journal of Supercritical Fluids,2008,45(3):338-345.
[30]SINTHUWAT R,REINHARD W,ALLAN S,et al. Selectivity and stability of alkaline protease AL-89 in hydrophilic solvents[J]. Journal of Molecular Catalysis B:Enzymatic,2009,59(4):266-273.
[31]MOHAMED G M. Preparation of sucrose fatty acid esters as food emulsifiers and evaluation of their surface active and emulsification properties [J]. Grasasy Aceites,1999,50(4):280-282.
[32]YASUAKI K,NOBUYUKI K,HIROSHI Y,et al. Process for producing sucrose fatty acid ester:US,5565557[P]. 1996-10-15.
[33]全国食品添加剂标准化技术委员会. GB 8272-2009 食品添加剂 蔗糖脂肪酸酯[S]. 北京:中国标准出版社,2009.
[34]ZHU Jin-li,TANG Yan-feng,LI Jian-hua,et al. Analysis of sucrose esters with long acyl chain by coupling of HPLC-ELSD with ESI-MS system [J]. Chinese Journal of Chemical Engineering,2009,17(6):1032-1037.
[35]JAVIER F,HAROLD E S. Interaction of sucrose ester with casein micelles as characterized by size-exclusion chromatography[J]. Journal of Dairy Science,1995,78(12):2660-2665.
[36]FANUN M,WACHTEL E,ANTALEK B,et al. A study of the microstructure of four-component sucrose ester microemulsions by SAXS and NMR[J]. Colloids and Surfaces A:Physicochemical and Engineering Aspects,2001,180(1/2):173-186.
[37]MOLINIER V,FENET B,FITREMANN J,et al. Concentration measurements of sucrose and sugar surfactants solutions by using the ^{1}H NMR ERETIC method[J]. Carbohydrate Research,2006,341(11):1890-1895.