Synthesis and Surface Activities of a Silicone Based Ester Quaternary Amine and Optimization of Synthesis Conditions by Response Surface Method

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Abstract: A novel silicone based ester quaternary ammonium salt (Si-QAS) was synthesized by conjugation of γ-chloropropyl methyl dimethoxysilane and distearic ester of methyldiethanolamine. The chemical structure of the Si-QAS was characterized by using FTIR and ^{1}H NMR. Physicochemical properties of the compound were further investigated and the results showed that the critical micelle concentration of the esterquat was 2.36×10^{-4} mol.L^{-1}, the corresponding surface tension γ_{CMC} was 24.25 mN.m^{-1}, and the standard Gibbs free energy of formation for micellization and adsorption were -30.64 kJ.mol^{-1} and -56.87 kJ.mol^{-1}, respectively. A mathematical model based on the method of response surface was also established to optimize the conditions of the synthesis process. Microwave power was found to have the strongest effect on synthesis progress and the optimal synthesis conditions were microwave power at 600 W for 20.89 min with a solvent amount of 9.24 g.

Keywords: Silicone ester quaternary amine, Si-QAS surface activity, γ-chloropropyl methyl dimethoxysilane, distearic ester methyldiethanolamine, response surface method.

1. INTRODUCTION

In recent decades, the development and use of green chemicals for textile and fabric industries have received much attention. Products such as ester quaternary amines (esterquats) that are readily biodegradable and environmentally friendly are the main focus. Esterquat surfactants can be easily decomposed by bacteria in the environment and rapidly degraded into aliphatic acids and small cationic metabolites in wastewater due to the introduction of weak ester bond in the molecular structure [1-3]. Organosilicon quaternary ammonium salts (Si-QAS) are excellent fabric finishing agents with properties that can not only make the fabrics to acquire good antibacterial properties, but also good fabric performance in terms of water absorption, perspiration absorption, pliability, gliding property, and elastic resilience [4-5]. By using silane coupling agent instead of traditional reagents such as alkyl halide and dimethylsulfate, Si-QAS inherits both the advantages of organosilicones and hydrocarbon surfactants to combine with fabrics with covalent bonds and electrostatic interaction. Therefore, Si-QAS surfactants suggest a new direction in the development of finishing agents for fabrics with antistatic properties, perfect softening effect, non-toxic and durable antibacterial properties. However, the synthesis process of Si-QAS is complicated and expensive. There are few reports on the synthesis of silicone based esterquat surfactant by using silane coupling agents and bi-long chain ester amines [6].

The response surface method is a method of statistical analysis that can be used to optimize the progress of surfactant synthesis [7-8]. By establishing a continuous variable surface model, every effect factor related to the progress and their interactions can be evaluated to determine the optimum range of the parameters. When compared with the method of orthogonal design, response surface method requires fewer experimental data and it is more intuitive to reflect the optimal values of dependent variable [9-11].

In this paper, a novel silicone based esterquat was synthesized under microwave irradiation by using γ-chloropropyl methyl dimethoxysilane and distearic ester of methyldiethanolamine. The surface activities of the synthesized esterquat were also characterized and the pH stability of the final product evaluated. The method of response surface was used to establish a central-composite model to determine the optimal synthesis conditions for solvent dosage, microwave power and reaction time.

2. MATERIALS AND METHODS

2.1. Materials

Distearic ester of methyldiethanolamine (98%) was synthesized as in previous work [12]. Other reagents

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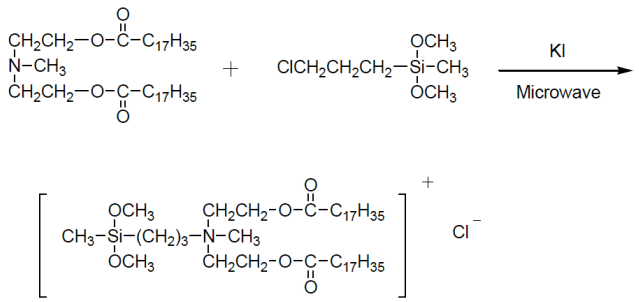
E-ISSN: 2410-3624/17

were purchased from various sources as follows: γ-Chloropropyl Methyl Dimethoxysilane (AR, Junye Corporation, Guangzhou); Dimethyl sulfoxide (DMSO, AR, Damao Corporation, Tianjin); Potassium iodide (AR, Guanghua Chemical Corporation, Shantou); Perchloric acid, absolute ether, glacial acetic acid, acetic anhydride, crystal violet (AR).

2.2. Synthesis and Identification of Si-QAS

The Si-QAS was synthesized as follows: 13.02 g of distearic ester of methyldiethanolamine were dissolved in 9.25 g DMSO, and into the mixture, 5.475 g of γ-chloropropyl methyl dimethoxysilane and 0.166 g of KI were added. The mixture was then heated with a microwave power for 15—25 min under nitrogen atmosphere. The reaction mixture was cooled down to room temperature and eluted with absolute ether several times. The precipitate was collected by centrifugation as a brown solid to be the final product. The product yield was about 50%. The synthesis route was shown in Scheme **1**. The synthesized Si-QAS was fully identified by FTIR and ^{1}H NMR.



Scheme 1: Synthesis Route of Ester of Organosilicon Quaternary Ammonium Salt.

2.3. Methods of Analysis

The infrared absorption spectrum was obtained by using a Fourier transform infrared spectrometer (TENSOR27, BRUKER Corporation). The ^{1}HNMR spectrum was obtained by using a nuclear magnetic resonance spectrometer (600MHzDD2(DirectDrive2), Agilent Corporation). The surface tension of surfactant solutions was measured with an automatic interface tension meter (BZY-1, Hengping Corporation).

2.4. Physicochemical Property Analysis

The surface tensions of the solutions of the Qi-QAS were measured in double distilled water solutions at 25°C for more than 15 min. The surface tension of the disltilled water was 72.3 mN·m^{-1}. The critical micelle concentration (CMC) was determined from the surface tension – concentration curve (at the turning point). The minimum surface area of the surfactant at interface (A_{min}), standard Gibbs free energy for formation of micellization (ΔG_{mic}) and adsorption (ΔG_{ads}) were calculated from the followings [13]:

$$\Gamma_{max} = \frac{-1}{RT}\left(\frac{d\gamma}{d\ln C}\right) = \frac{-1}{2.303RT}\left(\frac{d\gamma}{d\lg C}\right) \quad (1)$$

$$A_{min} = \frac{10^{16}}{N_A \Gamma_{max}} \quad (2)$$

$$\Pi_{CMC} = \gamma_0 - \gamma_{CMC} \quad (3)$$

$$\Delta G^0_{mic} = RT \ln CMC \quad (4)$$

$$\Delta G^0_{ads} = \Delta G^0_{mic} - \Pi_{CMC} A_{min} \quad (5)$$

where Γ_{max} is maximum adsorption at saturation (mol·cm^{-2}), R is the universal gas constant (8.314 J·mol^{-1}·K^{-1}), T is thermodynamic temperature (K), γ is surface tension of the solution (mN·m^{-1}), γ_0 is the surface tension of water at 25 °C, Π_{CMC} is the difference between γ_0 and γ_{CMC}, C is surfactant concentration (mol·L^{-1}), N_A is the Avogadro constant (6.02×10^{23}mol^{-1}).

The pH stability of the surfactant solution were observed by measuring the surface tension at a concentration of 0.1% at 25°C under the pH range of 2–12 at different time intervals.

3. RESULTS AND DISCUSSION

3.1. Characterization of Chemical Structure

The chemical structure of the synthesized Si-QAS was characterized with FTIR and ^{1}HNMR spectrum analysis (Figure **1** and **2**). From the analysis, the following spectrum peaks and their corresponding functional groups were identified. IR (KBr, v, cm^{-1}): 2919-2855 cm^{-1} (C-H), 1733 cm^{-1} (C=O), 1159 cm^{-1} (O-C=O), 721 cm^{-1} ($(CH_2)_n$, n>7), 952 cm^{-1} (N^+), 1259 cm^{-1} (Si-CH_3), 1100 cm^{-1} (Si-O); ^{1}HNMR ($CDCL_3$, 400MHz, ppm): 3.43(Si-OCH_3), 0.12(Si-CH_3), 2.35(N-CH_3), 2.85(N-CH_2), 4.53(N-C-CH_2), 3.37(Si-C-C-CH_2), 0.64(Si-CH_2). Therefore, it can be considerd that the target compound as indicated in Scheme 1 was fully identified and confirmed.

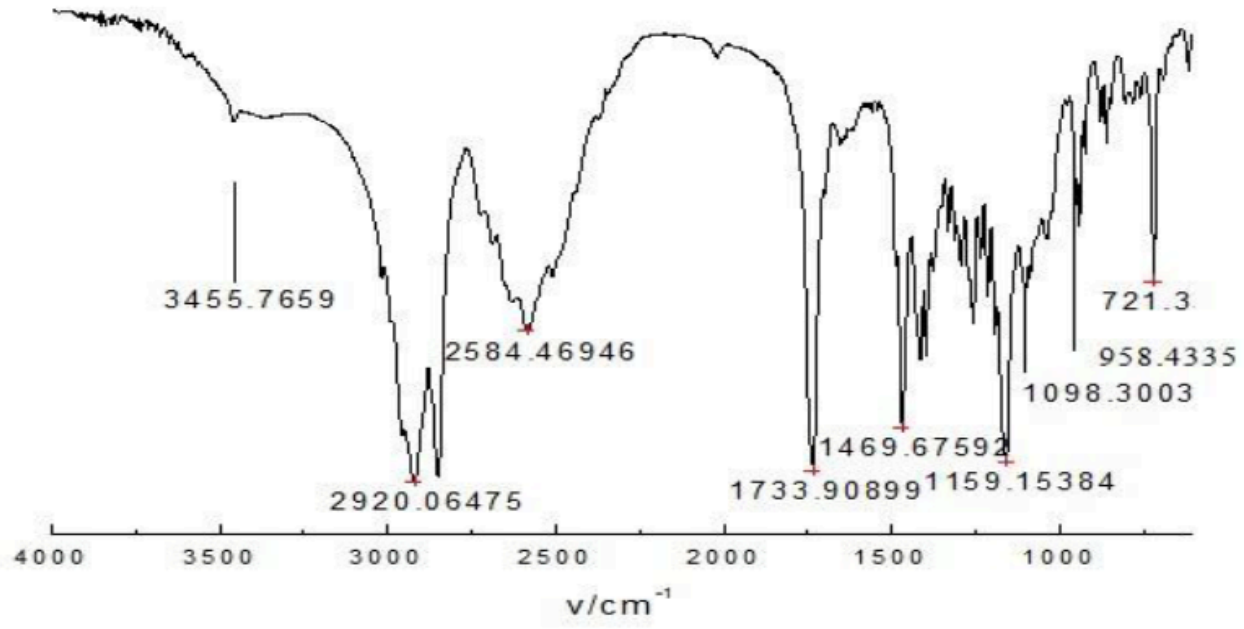


Figure 1: FTIR spectrum of synthesized product.

Table 1: Parameters of Micellization and Adsorption at 25 °C

Surfactant	CMC ($mol \cdot L^{-1}$)	γ_{CMC} ($mN \cdot m^{-1}$)	Π_{CMC} ($mN \cdot m^{-1}$)	Γ_{max} ($mol \cdot cm^{-2}$)	A_{min} (nm^2)	ΔG_{ads} ($KJ \cdot mol^{-1}$)	ΔG_{mic} ($KJ \cdot mol^{-1}$)
Si(1)-QAS	2.36×10^{-4}	24.25	47.72	1.82×10^{-10}	91.27	-56.87	-30.64
Si(3)N-LA	1.03×10^{-3}	21.00	51.30	2.54×10^{-10}	65.3	-47.1	-27.0

3.2. Micellization and Adsorption Properties

The surface tension – concentration relation curve is shown in Figure **1**. The surface tension of the solution decreased as the concentration in solution increased. This phenomenon indicated that the surfactant molecules were tightly arranged on the surface of the solution, and the surface tension was balanced after reaching CMC value. Results in Figure **1** also indicated that this compound was an efficient surfactant that reduced the surface tension of water to below 25 $mN \cdot m^{-1}$. This compares favorably to 30 – 40 $mN \cdot m^{-1}$ for hydrocarbon surfactants.

The parameters of micellization and adsorption of the esterquat and another surfactant trisioxane are given and compared in Table **1**. The minimum area occupied per esterquat molecule in Table **1** is larger than that of trisiloxanes. In addition, the values of ΔG_{mic} and ΔG_{ads} are negative, and therefore it can be concluded that micelle formation in water was spontaneous. The results also showed that ΔG_{ads} < ΔG_{mic}, indicating that adsorption is a more favorable process than the micellization process.

3.3. pH Stability

The surface tension of the surfactant solution at the concentration of 0.1% obtained at the pH range of 2 – 12 under different time intervals are shown in Figure **2**. The results show that the surface tension of solution within the pH range was largely unchanged (γ_{CMC} < 30 $mN \cdot m^{-1}$). The Si-QAS surfactant showed stability in the neutral and weak alkaline solutions, which was similar to similar surfactants reported [14-15]. On the other hand, in the strongly acidic and strongly basic solution, the stability of the Si-QAS in much better [16]. Therefore, it can be considered that the Si-QAS has application in a wide range of pH ranges.

3.4. Response Surface Analysis

In the analysis by using the method of response surface, solvent dosage ($\mathbf{X_1}$), microwave power ($\mathbf{X_2}$)

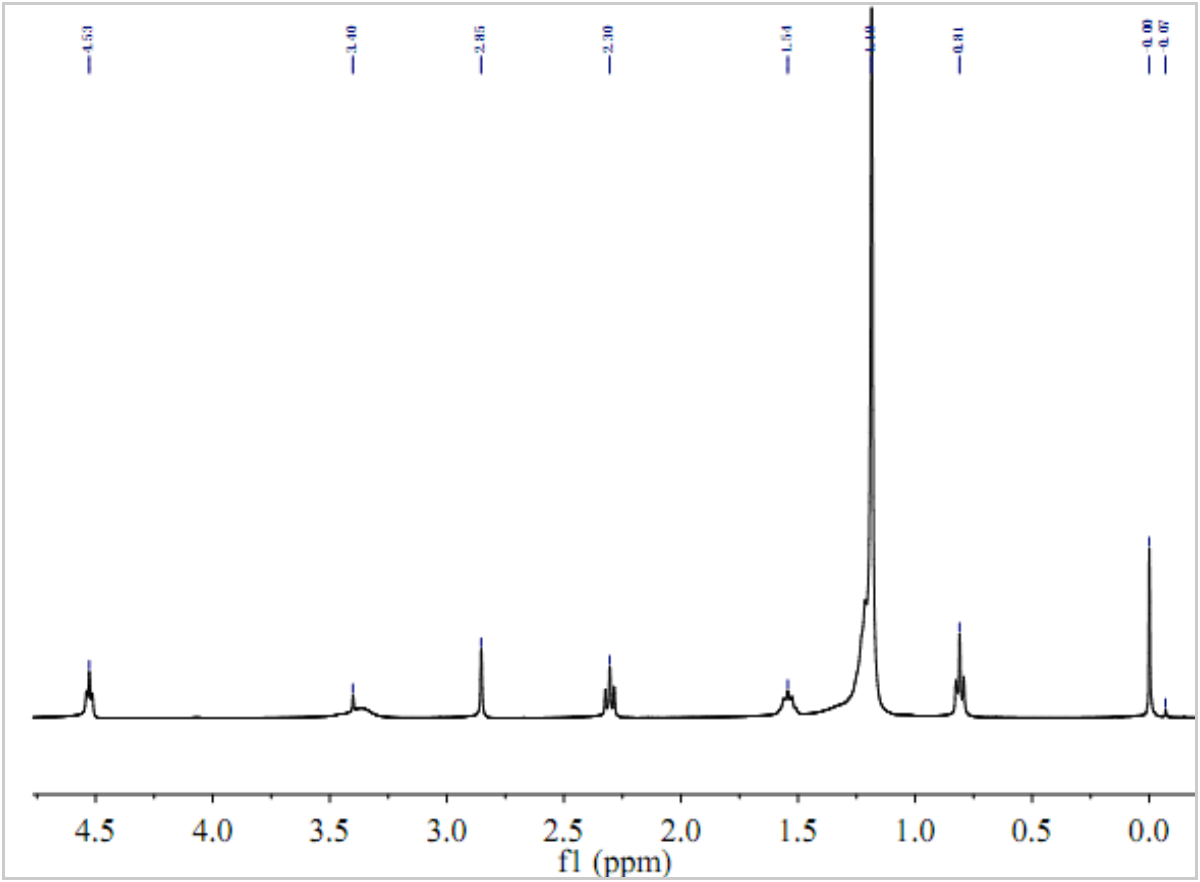


Figure 2: ^{1}HNMR spectrum of synthesized product.

Table 2: Experimental Design of Three Factors and Three Levels of Response Surface

Factor		Level	
	-1	0	1
X_1 : solvent dosage/g	7.40	9.25	11.10
X_2 : react time/ min	15	20	25
X_3 : microwave power/W	400	500	600

and reaction time (**X_3**) were used as three independent variables (factors) to establish the regression model to optimize the synthesize of the Si-QAS. The experimental designs are given in Table **2**.

The fractional conversion rate of distearic ester of methyldiethanolamine was used as the response parameter and the parameter values are given in Table **3**.

A quadratic regression analysis was then carried out and the multiple regression equation was generated as shown in below:

$$Y=44.24+O.58X_1+1.96X_2+9.56X_3-0.7X_1X_2-0.48X_1X_3-0.32X_2X_3-3.69X_1^2-4.58X_2^2+2.64X_3^2 \quad (2)$$

A variance analysis was carried out for the regression equation and the results are given in Table **4**. The P value was obtained to be less than 0.0001, indicating that the model equation was statistically significant. The factor of microwave power was determined to have the strongest effect on statistical significance, followed by reaction time and solvent dosage. Furthermore, the lack of fit P was 0.8825 and coefficient of determination R^2 was 0.9949, indicating a high reliability of the regression model.

Table 3: Central Composite Design and the Experimental Results

No.	X_1	X_2	X_3	Conversion Ratio/%
1	9.25	20	500	44.65 42.89 44.59 44.55 44.28 44.61 37.96 50.69 41.27 47.47 32.04
2	9.25	20	500	42.89 44.59 44.55 44.28 44.61 37.96 50.69 41.27 47.47 32.04
3	9.25	20	500	44.59 44.55 44.28 44.61 37.96 50.69 41.27 47.47 32.04
4	9.25	20	500	44.55 44.55 44.28 44.61 37.96 50.69 41.27 47.47 32.04
5	9.25	20	500	44.28 44.55 44.28 44.61 37.96 50.69 41.27 47.47 32.04 42.89 44.59 44.55 44.28 44.61 37.96 50.69 41.27 47.47 32.04
6	9.25	20	500	44.61 42.89 44.59 44.55 44.28 44.61 37.96 50.69 41.27 47.47 32.04

7	9.25	15	500	37.96 42.89 44.59 44.55 44.28 44.61 37.96 50.69 41.27 47.47 32.04
8	7.40	25	600	50.69 42.89 44.59 44.55 44.28 44.61 37.96 50.69 41.27 47.47 32.04
9	9.25	25	500	41.27 42.89 44.59 44.55 44.28 44.61 37.96 50.69 41.27 47.47 32.04
10	11.10	15	600	47.47 42.89 44.59 44.55 44.28 44.61 37.96 50.69 41.27 47.47 32.04
11	11.10	25	400	32.04 42.89 44.59 44.55 44.28 44.61 37.96 50.69 41.27 47.47 32.04
12	11.10	25	600	49.01
13	7.40	25	400	30.83
14	11.10	20	500	41.06
15	7.40	20	500	39.94
16	11.10	15	400	28.24
17	9.25	20	600	56.49
18	7.40	15	400	25.19
19	7.40	15	600	45.37
20	9.25	20	400	37.17

Table 4: Analysis of Variance and Significance Test of the Regression Model

Source	Sum of squares	Degree of freedom	Mean Square	*F*-value	Prob>*F*
Model	1140.19	9	126.69	409.71	< 0.0001
X_1	3.36	1	3.36	10.88	0.0080
X_2	38.46	1	38.46	124.36	< 0.0001
X_3	913.17	1	913.17	2953.2	< 0.0001
$X_1 X_2$	3.95	1	3.95	12.77	0.0051
X_1X_3	1.84	1	1.84	5.96	0.0348
X_2X_3	0.83	1	0.83	2.69	0.1320
X_1^2	37.55	1	37.55	121.42	< 0.0001
X_2^2	57.69	1	57.69	186.55	< 0.0001
X_3^2	19.09	1	19.09	61.75	< 0.0001
Residual	3.09	10	0.31	-	-
Lack of fit	0.75	5	0.15	0.32	0.8825
Pure error	2.34	5	0.47		
Cor total	1143.28	19			

The trend of isohypse reflects the mutual effect of two factors and they are shown in Figures **3-5**. An arc line means there is weak effect between two factors, and on the contrary, a flat line means there is a strong effect between two factors. As shown in Figure **3**, isohypse Y is nearly a sub-circular, which means an ordinary effect between X_1 and X_3. Parabola Y related to X_1 is steeper than the Y parabola related to X_3. This phenomenon illustrates that Y is directly proportional relationship to X_1 and X_3, and a stronger correlation with X_1. Y reached the maximum value in the range of 9.25 -10.17 g which is a highest paraboloid. This is mainly because of the fact that a moderate dosage of solvent can enhance the reaction rate of quaternization reaction.

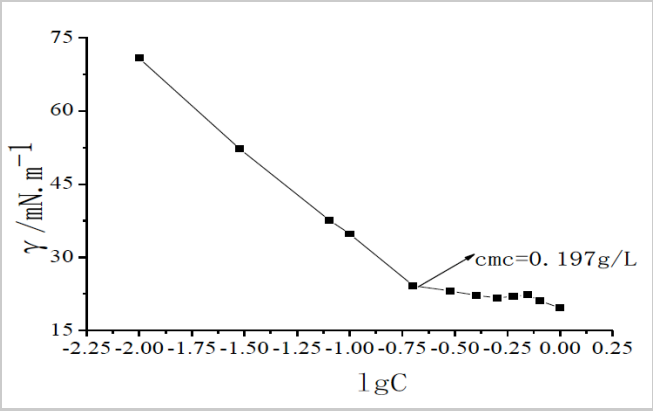


Figure 3: Surface tension (γ) – concentration (logC) relation curve of solutions of product.

Isohypse Y is also nearly a sub-circular in Figure **4**, which means the mutual effect between X_2 and X_3 can be ignored. Parabola Y as related to X_2 is steeper than the parabola Y as related to X_3. This phenomenon illustrates that Y has a direct proportional relationship with X_2 and X_3, and a stronger correlation with X_2. Y reached the maximum value in the range of 20.00-22.25 min, which is a highest paraboloid.

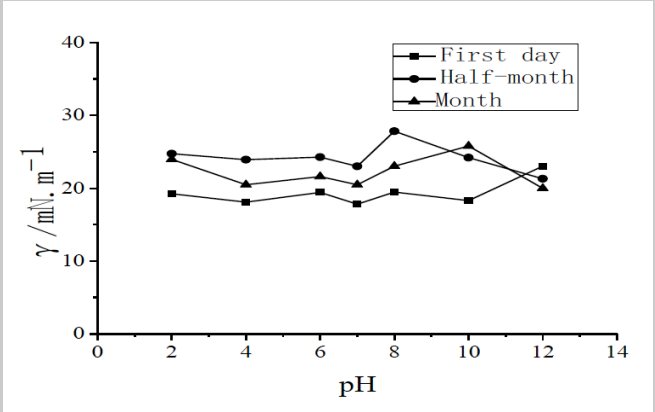


Figure 4: The stability of surfactant on different pH values.

Isohypse Y is nearly an oval in Figure **5**, which means the mutual effect between X_2 and X_3 is strong. Furthermore, with the increasing X_1 and X_2, the Y curve increases at first, then decrease. Y reached the maximum value in the range of 9.25-10.17g X_1, and parabola Y as related to X_2 is steeper than the parabola Y as related to X_1. This phenomenon illustrates that Y has a direct proportional relationship with X_1 and X_2, and a stronger correlation with X_2.

3.5. Model Validation

From the above analysis, it can determined that the optimal reaction conditions were as follows: microwave power at 600 W for 20.89min with a solvent dose of 9.24 g. Under these conditions, the optimal fractional

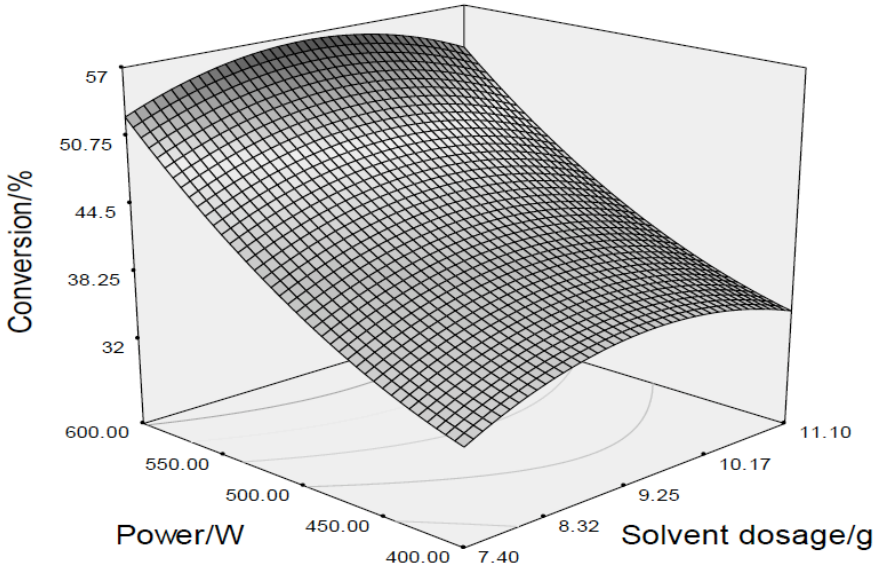


Figure 5: Response surface plotted on microwave power and solvent dosage.

conversion rate was 57.25%. This result was validated by carrying out three experiments under the optimal conditions and the average conversion rate obtained was 57.05%, which was close to the predicted value of 57.25%. This suggests that it is feasible to use response surface method to optimize the synthesis conditions [17-19].

CONCLUSIONS

A novel silicone based ester quaternary ammonium salt (Si-QAS) was synthesized by conjugation of γ-chloropropyl methyl dimethoxysilane and distearic ester of methyldiethanolamine. The surfactant showed a good performance in reducing surface tension and stability in a wide range of pH. The critical micelle concentration of the prepared esterquat was determined to be 2.36×10^{-4} $mol.L^{-1}$, the corresponding surface tension γ_{CMC} was 24.25 $mN.m^{-1}$, and standard free energy of formation for micellization and adsorption were -30.64 $kJ.mol^{-1}$ and -56.87 $kJ.mol^{-1}$, respectively. A mathematical model based on the method of response surface was also established to optimize the conditions of the synthesis process. Microwave power was the factor that has the strongest effect on synthesis progress, followed by reaction time and solvent dosage. The optimal synthesis conditions were microwave power at 600 W for 20.89 min with a solvent amount of 9.24 g.

REFERENCES

[1] Miao ZC, Yang JZ and Wang L. Synthesis of Biodegradable Lauric Acid Ester Quaternary Ammonium Salt Cationic Surfactant and Its Utilization as Calico Softener. Mater Lett 2008; 62: 3450-3452. https://doi.org/10.1016/j.matlet.2008.02.084

[2] Bahmaei M, Badiee F and Kasehgari H. Synthesis, IR, HPLC Analysis and Performances of Palm Fatty Acids and Triethanolamine-Based Esterquats. J Surfactants Deterg 2011; 14:173-177. https://doi.org/10.1007/s11743-010-1218-3

[3] Achouri ME, Alehyen S and Assioui A. Synthesis and Physico-Chemical Studies of Ester-Quat Surfactants in the Series of (Dodecanoyloxy) propyl n-Alkyl Dimethyl Ammonium Bromide. J Surfactants Deterg 2013; 16: 473-485. https://doi.org/10.1007/s11743-013-1455-3

[4] Salman M, Athar M and Shafique U. Microwave Assisted Synthesis of Esterquat for Fabric Softening Applications. J Chem Soc Pak 2012; 34: 415-418.

[5] Li YL, Li QX and Zhi LF. Synthesis, Characterization and Surface-Activity of Hydroxyethyl Group-Containing Quaternary Ammonium Surfactants. J Surfactants Deterg 2011; 14: 529-533. https://doi.org/10.1007/s11743-011-1279-y

[6] Xu Q, Jiang B and Zhan XL. Study on Solvent Effect on Quaternization of γ-chloropropyl Trimethoxy Siloxane. J Chem Eng Chin Uni(China)2007; 21: 640-644.

[7] Zhu XH, Yang C and Chen G. Microwave-Assisted Synthesis of Siloxane Quaternary Ammonium Salts. Acta Sci Nat Uni Sunyatseni(China) 2009; 48: 56-59.

[8] Huang WH, Zheng C and Mao TY. Synthesis and Characterization of Silicone Based Esterquat for Fabric Softening Application. Fine Chem (China) 2012; 12: 1167-1171.

[9] Bezerra MA, Santelli RE and Oliveira EP. Response Surface Methodology (RSM) as A Tool for Optimization in Analytical Chemistry. Talanta 2008; 76: 965-977. https://doi.org/10.1016/j.talanta.2008.05.019

[10] Tan IAW, Ahmad AL and Hameed BH. Optimization of Preparation Conditions for Activated Carbons from Coconut Husk Using Response Surface Methodology. Chem Eng J 2008; 137: 462-470. https://doi.org/10.1016/j.cej.2007.04.031

[11] Wei YL and Zheng C. Microwave Synthesis Optimization, Structure and Properties of CTA J. J Chem Ind and Eng (China) 2009; 60: 2130-2136.

[12] Huang WH, Zheng C, Mao TY, Lin J, Yu XH, *et al*. Synthesis and Characterization of Silicone Based Esterquat forFabric Softening Application, Fine Chemicals(China) 2012; 29: 1167-1172.

[13] Mohamed MZ and Mohaned AS. Synthesis and Some Properties of Fluorinated Cationic Surfactants. J Surfactants Deterg 2009; 12: 345-349. https://doi.org/10.1007/s11743-009-1126-6

[14] Chlebicki J, Wegrzyńska J and Wilk KA. Surface-active, Micellar, and Antilectrostatic Properties of Bis-Ammonium Salts. J Colloid Interface Sci 2008; 323: 372-378. https://doi.org/10.1016/j.jcis.2008.04.011

[15] Yin DN, Zheng C and Zhang LP. Synthesis and Characterization of Polyether Modified Trisiloxanes. CIESC Journal 2010; 61: 1565-1570.

[16] Cheng WJ, Zheng C and Mao TY. Microwave Synthesis Technique and Properties of Octadecylmethyldihydroxyethyl Ammonium Bromide. J Chem Ind Eng (China) 2011; 62: 566-573.

[17] Cheng WJ. Synthesis and Properties of Octadecylmethyldihydroxyethyl Ammonium Bromide. MS Thesis, Guangzhou University, Guangzhou, PR China 2011.

[18] Fu H and Zhang GY. Synthesis and Characterization of Glucosamide-Based Trisiloxane Gemini Surfactants. J Surfactants Deterg 2004; 7 :175-180. https://doi.org/10.1007/s11743-004-0301-2

[19] Murata H1, Koepsel RR, Matyjaszewski K and Russell AJ. Permanent, Non-Leaching Antibacterial Surfaces-2: How High Density Cationic Surfaces Kill Bacterial Cells. Biomaterials 2007; 28: 4870-4879. https://doi.org/10.1016/j.biomaterials.2007.06.012

Received on 20-12-2017 Accepted on 27-12-2017 Published on 31-12-2017

DOI: http://x.doi.org/10.15377/2410-3624.2017.04.4