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ORIGINAL ARTICLE

Quantitative Monitoring of the Amidation Reaction Between Coconut Oil and Diethanolamine by Attenuated Total Reflectance Fourier Transform Infrared Spectrometry

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Abstract An analytical procedure was developed to monitor the batch reaction of coconut oil and diethanolamine which also would determine the cocodiethanolamide (CDEA) content of the final product. The method was based on attenuated total reflectance Fourier transform infrared spectrometry utilizing partial least squares regression. The calibration was modeled in the 1,781–1,714 and 1,658–1,639 cm^{-1} spectral regions for coconut oil and CDEA respectively. The models were then applied to predict the amidation process yield and to monitor the in situ kinetics of reactions between coconut oil and DEA. The root mean square error of prediction was 0.590 and 0.336 for coconut oil and CDEA respectively. The proposed method can also be successfully applied to the determination of purity in commercial grade CDEA samples and would give reliable results in comparison with the potentiometric titration reference method.

Keywords Amidation · Cocodiethanolamide · ATR-FTIR spectrometry · Partial least squares · Quantitative · Monitoring

Abbreviations

ATR-FTIR	Attenuated total reflectance Fourier transform infrared spectrometry
CDEA	Cocodiethanolamide
DEA	Diethanolamine
PLS	Partial least square

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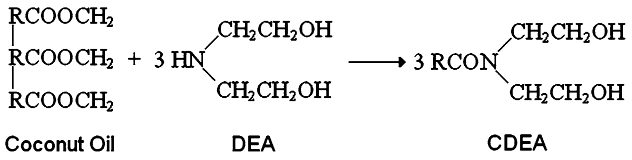
Introduction

Cocodiethanolamide (CDEA)—also known as cocamide diethanolamine with chemical formula of RCON(CHB$_{2B}$ CHB$_{2B}$OH)B$_{2B}$, where R is linear alkyl chain with 7–17 carbons, is a nonionic secondary surfactant which is used as an excellent viscosity enhancing and foam stabilizing agent in anionic-based products, e.g., hand washing liquids, shampoos, body lotions and wetting agents. Its good emulsifying properties also make it suitable for application in the field of pharmaceutical, agricultural preparations and textile processing, and for rust inhibiting, latex stabilizing, antistatic function, dye leveling, water proofing and water-in-oil additives.

CDEA is the condensation product of the reactions between diethanolamine (DEA) and coconut fatty acid, coconut oil or methyl ester of coconut oil (Scheme 1). In this study coconut oil was used as the starting fatty material, glycerin was also the byproduct. The typical composition of the product consists of 80–85% CDEA, $>5\%$ free DEA, trace amounts of fatty acid soap and other by products. The reaction is relatively mild and proceeds readily using 0.2–0.3% sodium methylate at an operating temperature (70–100 °C) and at atmospheric pressure [1]. To ensure good properties, the reaction must be carried out under optimal condition because the presence of unreacted coconut oil and reaction intermediates degrades the performance of the CDEA. Some disadvantages of incomplete process are further reducing foam and raising the cloud point, which cause some problems to attain a clear transparent product. Therefore it is necessary to monitor the amidation process.

Several analytical methods have been introduced for quantitative determination of CDEA in industrial and commercial grade samples. Some reported in the literature



Scheme 1 Amidation reaction of coconut oil with diethanolamine

include potentiometric titration [2], high performance liquid chromatography [3, 4], gas chromatography [5, 6] and capillary electrophoresis [7]. Classic analytical procedures and chromatographic techniques are time-consuming and require several chemical reagents and solvents which increase the costs of analysis besides being harmful to the environment. FTIR spectrometry is a fast analytical technique which provides useful qualitative and quantitative information. Application of attenuated total reflectance (ATR) would develop the use of infrared spectroscopy by simplifying sample handling and avoiding common operating problems in the transmission mode, e.g., cell filling and cleaning or variation of the path length due to window wear [8]. During the last decade, many researchers have applied chemometrics to analytical models based on FTIR spectrometry. Among chemometric methods, partial least squares (PLS) has been frequently used because of the quality of calibration models obtained, the ease of its implementation and the availability of software. PLS is used to extract the relevant part of information and produce reliable models [9, 10]. In the present work a procedure has been developed to monitor the progress of the amidation reaction of coconut oil and DEA via determination of CDEA content of the final product. ATR-FTIR spectrometry data have been processed by the PLS technique. Easy sample preparation, rapid analysis and accurate results are the main advantages of the proposed method.

Experimental

Chemical Reagents, Apparatuses and Software

Refined RDB® coconut oil (bleached and deodorized) was obtained from Cargil Palm Products (Selangor, Malaysia)and it contained 0.016% (w/w) of free fatty acids and 0.019% (w/w) moisture. Cocodiethanolamide was AMIDET B-112 (92% CDEA) purchased from Witco surfactants. Glycerin, diethanolamine and isopropanol were of analytical grade (Merck®, Germany). Also, all chemical reagents, used in the reference method: perchloric acid (70–72%), potassium hydrogen phthalate, glacial acetic acid and acetic anhydrides, were all of analytical grade (Merck®, Germany).

A Magna 550 FTIR Spectrometer (Nicollet, Madison USA) equipped with a DTGS detector, an Ever-Glo source and a CSI beam splitter, was employed for spectral analysis. A horizontal SpectraTech® ATR cell equipped with a 45° ZnSe trough plate was applied. Omnic® QuantIR software was used to process the absorbance data, performing a PLS algorithm. Potentiometric titrations were carried out using a Metrohm® (Model 726) titroprocessor.

Synthesis

A batch of coconut oil (66 g) and DEA (31.5 g) were placed in a round-bottomed flask with the addition of a catalyst (0.25% w sodium methylate) and agitated. The temperature of the reactor was increased to 75 ± 2 °C (at atmospheric pressure). The reaction was carried out for 2 h. At different reaction times (15, 30, 60, 90, and 120 min), about 3 g of sample was taken from the reactor and immediately immersed in ice to arrest the reaction rate. Each sample was dissolved in isopropanol to achieve an approximately 15% w/w solution. The samples were analyzed in the same day in which reaction was performed.

Reference Method for Determination of CDEA in Commercial Grade Samples

First, about 5 g of sample was weighed and dissolved in glacial acetic acid and then titrated potentiometrically with 0.1 M perchloric acid in glacial acetic acid. Then, about 0.7 g of the sample was weighed and dissolved in acetic anhydride and then titrated potentiometrically with 0.1 M perchloric acid in glacial acetic acid. The end points of titration curves were detected with a modified calomel–glass electrode couple. Titration of the sample in glacial acetic acid gives basicity due to DEA, while titration in acetic anhydride determines total basicity. The difference represents the amide content. The equation for quantitative determination of CDEA is:

$$\text{CDEA}\ (\%\ \text{w/w}) = \left(\frac{N \times V_2}{m_2} - \frac{N \times V_1}{m_1}\right) \times \frac{M_W}{10}$$

where N is normality of perchloric acid (eq lit^{-1}); V_1 is the consumed perchloric acid (ml) in the first step; V_2 is the consumed perchloric acid (ml) in the second step; m_1 is the mass of sample in the first step (g); m_2 is the mass of sample in the second step (g); M_W is the molecular weight of CDEA (g mol^{-1}).

Sample Preparation

Thirty-four standard solutions of coconut oil (2.53–24.73% w/w) and CDEA (1.39–21.50% w/w) were prepared in isopropanol solvent. In order to decrease the interfering effect, other components were added to the standard samples in different concentration levels (2.85–12.03% w/w for DEA and 1.65–6.58% w/w for glycerin).

The aforesaid standard solutions were applied in the calibration model, also for validating the model and for quantitative analysis of real samples.

Results and Discussion

Solvent Selection

A suitable solvent dissolves the analytical samples without reacting and has the least interference in the spectral region in which the analyte is investigated. In addition, it is better that it is not toxic. According to the high solubility of coconut oil, CDEA and other components in isopropanol, isopropanol was selected as an appropriate solvent in the proposed method. The ATR-FTIR absorbance spectra of isopropanol, coconut oil and CDEA in isopropanol with air and solvent background are shown in Figs. 1 and 2. As observed in Fig. 2, some useful signals appear in the spectra, setting solvent as the background.

Spectral Interpretation

As can be observed in Fig. 2, coconut oil and CDEA demonstrate intensive signals at 1,747 and 1,628 cm^{-1} respectively, which is attributed to the C=O stretching. There are also some quite considerable signals for both compounds at 2,925 and 2,855 cm^{-1}, which can be assigned to the asymmetric and symmetric stretching vibration of the methylene groups. Because of the long chain, the corresponding stretching vibration of the methyl groups at 2,960 and 2,875 cm^{-1} appear only subordinately or as shoulders of the methylene bonds [11]. Investigating the mentioned spectral data during the amidation reaction, the most significant change would occur in the 1,800–1,550 cm^{-1} spectral region, corresponding to relocation of the C=O stretching vibration from 1,747 cm^{-1} (ν C=O in triglycerides) to 1,628 cm^{-1} (ν C=O in alkyl diethanolamides).

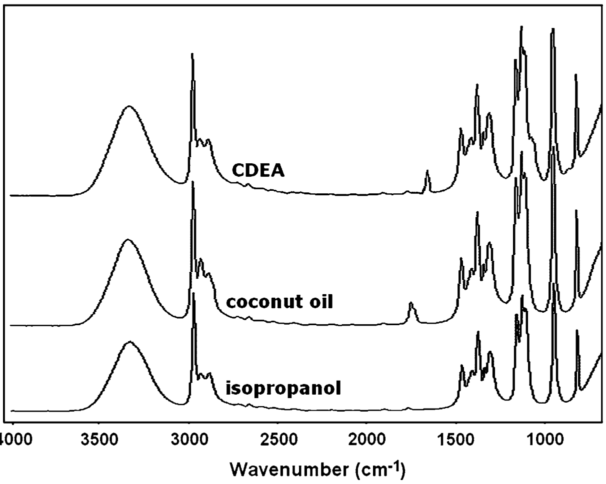


Fig. 1 ATR-FTIR spectra of solvent and analytes with an air background

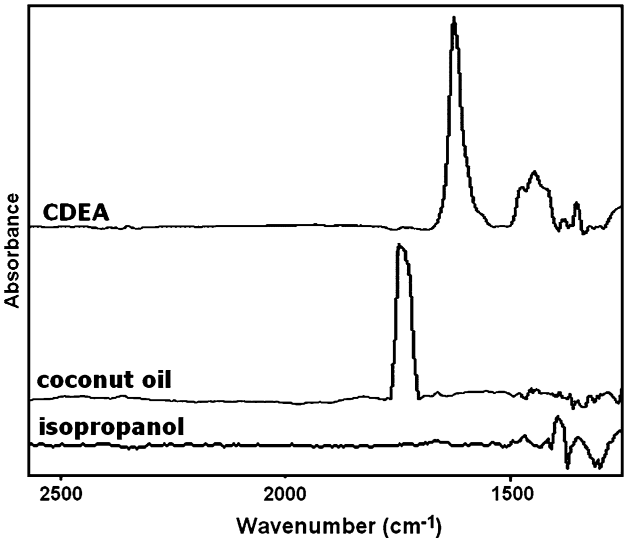


Fig. 2 ATR-FTIR spectra of solvent and analytes with a solvent background

Calibration Model and Validation Step

Multivariate calibrations are useful tools for use in spectral analysis in order to overcome the spectral problems and to improve the precision and the predictive ability of overlapping data in FTIR spectrometry. The PLS multivariate model was applied with the absorption spectra data. Spectral information was mean centered prior to PLS data treatment. The unique way to verify that one calibration model works well is to take new samples and predict them with the model. However, there are several choices for validation, including leverage correction, cross-validation using a small data set, leave-one out cross-validation and testing new samples. In this work, the leave-one out cross-validation was used. The basis of this method is that, the predictive ability of the formed model on part of dataset is tested out by how well it predicts the reminder of the dataset. The first 25 standard solutions (samples 1–25 in Table 1) were used to set up the calibration model and then the concentration of these samples was predicted by the leave-one out cross-validation process. The predicted results are also shown in Table 1. The calibration model was optimized by varying the number of PLS factors from 1 to 3. Cross-validation was also performed to select the optimum number of factors in the PLS algorithm. The prediction error sum of squares was calculated each time a new factor was added giving rise to different PLS models. One reasonable choice for the optimum number of factors would be that number (h*) which yielded the minimum

Table 1 Concentration of coconut oil and CDEA in calibration model (no. 1–25) and validation set (no. 26–34)

Sample	Actual (g per 100 g)		Predicted (g per 100 g)	
	Coconut oil	CDEA	Coconut oil	CDEA
1	2.53	1.48	2.88	1.38
2	2.78	6.42	2.91	6.55
3	2.60	11.98	2.49	12.47
4	2.74	16.63	2.71	16.97
5	2.59	21.18	2.28	20.8
6	7.91	1.51	8.18	1.41
7	8.07	6.64	8.11	6.76
8	8.48	11.74	8.30	11.92
9	8.00	16.56	8.31	16.63
10	8.24	21.48	8.32	21.35
11	13.04	1.39	13.35	1.18
12	13.30	6.61	13.42	6.99
13	12.92	11.49	12.81	12.01
14	13.13	16.72	12.80	17.40
15	12.98	21.34	12.42	21.41
16	18.96	1.45	19.37	1.03
17	19.14	6.73	19.30	6.63
18	19.05	11.69	18.98	11.96
19	19.11	16.82	18.93	16.53
20	19.32	21.39	18.90	20.87
21	24.73	1.46	25.39	1.12
22	24.50	6.50	24.93	6.42
23	24.41	11.77	24.30	11.90
24	24.65	16.80	24.35	16.83
25	24.53	21.50	23.95	20.81
26	10.20	17.46	10.76	17.19
27	4.95	13.02	4.28	12.89
28	16.48	3.45	17.27	3.55
29	9.21	12.51	9.45	12.72
30	15.85	8.45	17.03	8.91
31	4.63	17.51	4.32	17.06
32	2.86	13.21	2.59	13.49
33	4.63	17.67	4.31	17.24
34	2.82	13.25	2.60	13.18

Table 2 Selection of best spectral region for coconut oil modeling

	Spectral region (cm^{-1})			
	1,781–1,714	1,735–1,714	1,781–1,735	1,755–1,735
RMSEC[a]	0.314	0.317	0.315	0.764
R^2	0.992	0.992	0.992	0.994
RMSEP[b]	0.590	0.670	0.806	0.976

[a] Root mean square error of calibration

[b] Root mean square error of prediction

Table 3 Selection of best spectral region for CDEA modeling

	Spectral region (cm^{-1})			
	1,639–1,612	1,655–1,589	1,658–1,639	1,658–1,612
RMSEC[a]	1.240	0.460	0.321	0.399
R^2	0.985	0.987	0.990	0.991
RMSEP[b]	4.240	0.673	0.336	0.482

[a] Root mean square error of calibration

[b] Root mean square error of prediction

prediction error sum of squares. However, the best calibration model was obtained for the set of spectra with 1 PLS factor. With this ONF, the root mean square error of calibration was determined to be 0.314 and 0.321, while the correlation coefficient (R^2) was 0.992 and 0.990 for coconut oil and CDEA respectively. Different spectral regions were evaluated by performing PLS calibration method and finally, the 1,781–1,714 and 1,658–1,639 cm^{-1} spectral regions were selected as most convenient for coconut oil and CDEA respectively (Tables 2, 3). In order to ensure the accuracy of the calibration model, the remaining solutions (samples 26–34 of Table 1) were proposed as the independent test set to be predicted by the calibration model. The root mean square error of prediction was 0.590 and 0.336 for coconut oil and CDEA respectively.

Monitoring Progression of Amidation Reaction Between Coconut Oil and DEA

Five samples were collected at different time intervals from the batch reactor and dissolved in isopropanol (approximately 15% w/w). These solutions were analyzed by the proposed method, determining their coconut oil and CDEA content. Figure 3 shows the variation in analyte concentration in the reaction mixture versus time. The amidation reaction progressed rapidly in the first 15 min but thereafter slowed down. After 2 h, the CDEA concentration was raised to 82% and residual coconut oil was less than 4%. The results suggested the reaction time of 90 min as sufficient time for optimum formation of CDEA.

Comparison of ATR-FTIR Spectrometry with Titration Methods

Five commercial samples of CDEA supplied by Iranian manufacturers were analyzed by the proposed ATR-FTIR spectrometry to determine their amide contents. Samples 1 and 2 were Behdamid from Behdash Manufacturing Co. (Mahd-e-Taban Investment Co.). Samples 3, 4 and 5 were from Golshoo, Glan and Paxan companies respectively. In order to evaluate the accuracy and precision of the proposed method, these samples were also analyzed by the potentiometric titration method as the reference. Results are shown in Table 4. Generally good agreement

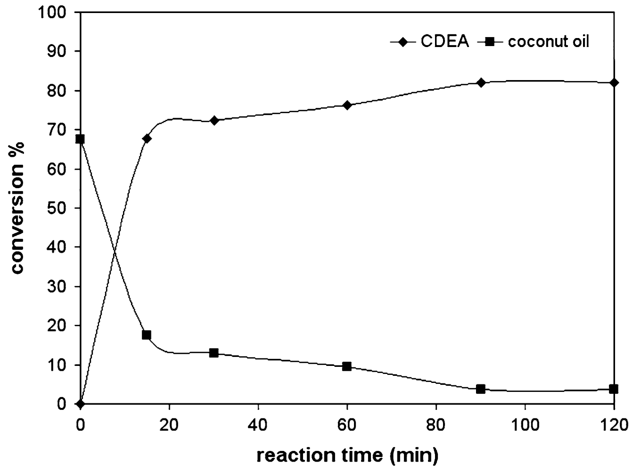


Fig. 3 Variations of main reactants during the amidation process, determined by ATR-FTIR spectrometry

Table 4 Determination of amide content in commercial grade CDEA samples by the reference and proposed methods (g per 100 g)

Sample	Reference method			Proposed method		
	Mean value[a]	SD[b]	RSD[c]	Mean value	SD	RSD
1	81.26	1.41	1.73	83.54	0.15	0.18
2	78.25	1.54	1.96	79.84	0.19	0.24
3	80.14	1.12	1.46	79.35	0.15	0.19
4	79.46	0.95	1.19	77.79	0.19	0.24
5	76.82	1.08	1.41	76.61	0.24	0.31

[a] Mean value of three measurements

[b] Standard deviation

[c] Relative standard error

was observed between two sets of results. As expected, the ATR-FTIR spectrometry method provided an accurate and precise route for the determination of CDEA in commercial grade real samples in the presence of matrix components.

The ATR-FTIR/PLS model applied in this study wasused to monitor the progression of amidation reaction coconut oil with DEA and to determine the amide content of the final product. This procedure is low-cost, accurate and environmental friendly as the amounts of organic solvents and chemical reagents used during quantitative determination process is reduced significantly. This method also suggests itself to be a powerful analytical procedure for the evaluation of many other amidation reactions because of its suitability to be implemented in on-line monitoring systems.

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