



STUDY OF THE REACTION FOR OBTAINING THE SUPRAMOLECULAR COMPOUND COCAMIDE DEA BY SPECTROPHOTOMETRIC METHOD

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ABSTRACT

In this work, the effect of solution acidity on the properties of diethanolamine cocamide was studied using a spectrophotometric method. Since solutions of the substance under study are colorless and, therefore, do not absorb light waves in the visible region of the spectrum, the study was carried out in the ultraviolet region. The possibility of interaction of diethanolamine cocamide with molybdenum polyoxometalates to obtain a supramolecular compound was investigated and the nature of the bond in the resulting compounds was determined. The results of these studies can be used in the development of new supramolecular substances based on cocamide diethanolamine for sensing environmental pollution.

Keywords: cocamide diethanolamine, cocodiethanolamide, coconut oil fatty acid diethanolamide, polyoxometalates, supramolecular compounds, spectrophotometry, surfactants.

Manuscript Received 7 July 2024; Revised 7 September 2024; Published 15 November 2024

INTRODUCTION

Supramolecules are large molecular structures consisting of individual molecules [1-5]. Unlike traditional chemistry, which focuses on covalent bonds between atoms, supramolecular chemistry studies non-covalent interactions between molecules themselves. These interactions lead to the self-assembly of molecules, which naturally form complex structures capable of performing various functions.

Cocamide diethanolamine (cocodiethanolamide, coconut oil fatty acid diethanolamide) is a mixture of fatty acid amides of coconut oil. Because coconut oil contains about 50% lauric acid, formulas typically only consider 12-carbon chains [6]. Therefore, the formula of cocamide is most often written as $\text{CH}_3(\text{CH}_2)_{10}\text{CONH}_2$, although the number of carbon atoms in the chains can be different [7].

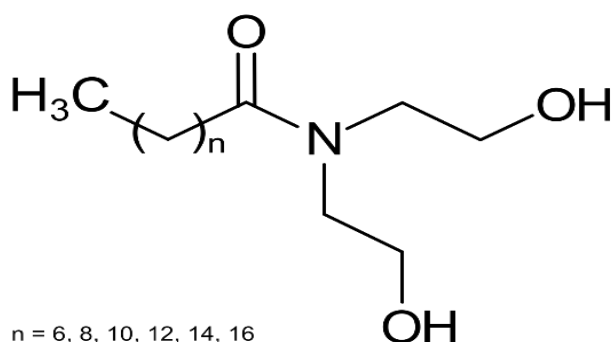


Figure-1. Cocodiethanolamide structural formula.

Cocamide is the structural basis of many surfactants. The most common are ethanolamines (monoethanolamine, diethanolamine, and triethanolamine cocamides) and betaine derivatives (cocamidopropyl betaine) [8]. Cocamide is used to improve foaming, as it

makes the foam thicker and more stable. Ego is also used to increase viscosity.

However, unlike most other nonionic surfactants, coconut oil diethanolamine does not have any emollient properties, but is a rather strong irritant. This divination at high concentrations can cause contact dermatitis.

According to the results of recent studies, it is considered to be 100% carcinogenic (according to the American Association of Cancer Research (AACR)). Based on the results of the studies and the statement of the AACR, this component was banned for use in some states, for example, in California. However, today this component is widely used in various foaming compositions, and therefore its release into the environment as a result of an accident at the factory or a terrorist attack on enterprises can have negative consequences, both for animals and for humans.

Polyoxometalates (POM) are complex and theoretically and practically interesting representatives of coordination compounds. They belong to poly-ligand inorganic compounds [9-10]. The most widespread analytical forms are the oxidized and reduced forms of polyoxometalates of the Keggin structure with the general formula $\text{XMe}_{12}\text{O}_{40}^{n-}$. Various POM salts of the composition $(\text{Kat}^+)_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ are characterized by good ion exchange properties. The results of previous studies indicate the possibility of obtaining electroactive supramolecular compounds based on molybdenum polyoxometalates and various organic substances [11-22]. The development of methods for the quantitative determination of organic pollutants using sensor systems of various types (electrochemical, fluorescent, luminescent, etc. [23]) that will allow rapid determination of the presence and concentration of pollutants in soil or drinking water is a promising direction in the development of alternative methods for determining the content of these substances. For the development of such sensory systems, various compounds, chemicals, and polyoxometalates are widely used [24-25], to eliminate inorganic-organic hybrid



compounds, which have a great potential for further stagnation in various species.

For this purpose, the possibility of chemical reactions between cocamide DEA and polyoxomolybdates to obtain electroactive supramolecular compounds was previously investigated, the nature of the bond in the resulting compounds was investigated, and the influence of various factors (for example, the acidity of the medium, the type of polyoxometalate) on the properties of the resulting supramolecular compound was studied.

MATERIALS AND DEVICES

Spectrophotometric studies were carried out with the spectrophotometer SF-46 (UV- spectra).

The following reagents are used in the work:

- polyoxomolybdate, $H_3PMo_{12}O_{40} \cdot x26H_2O$ (analytically pure);
- polyoxomolybdate, $H_5PMo_2Mo_{10}O_{40} \cdot x26H_2O$ (analytically pure);
- cocamide diethanolamine, $C_{12}H_{25}ON$ (analytically pure);
- sodium hydroxide (analytically graded);
- chloride acid (analytical grade).

EXPERIMENTAL PART

To determine the possibility of obtaining a supramolecular compound of the determined organic substance with polyoxomolybdate, it is necessary to study the nature of the interaction and determine rational conditions for the reaction.

To select rational conditions, the effect of solution acidity on the properties of cocamide diethanolamine was studied using a spectrophotometric method. Supramolecular complexes based on polyoxomolybdates cannot be obtained in highly alkaline solutions, since in this case the polyoxomolybdates can be destroyed to molybdenum oxide. Therefore, the spectral characteristics of solutions of cocamide DEA (SDEA) were recorded at the intrinsic acidity of the solution (pH = 6), in the weakly acidic (pH = 4) and alkaline (pH = 8-10) regions. Absorption spectra were recorded in the range of 200-350 nm in quartz glass cuvettes (solution layer thickness 1 cm). Distilled water was used as a solvent and reference solution in all analyzes (Figure-2).

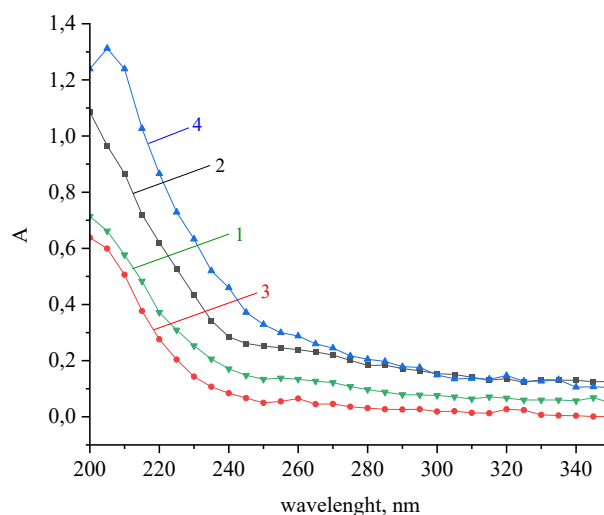


Figure-2. UV absorption spectrum of cocamide DEA at pH = 4 (1), pH = 6 (2), pH = 8 (3) and pH = 10 (4).

The obtained UV absorption spectra of coconut oil fatty acid diethanolamide aqueous solutions, regardless of solution acidity, show the absorption maxima of average intensity at a wavelength of 200-210 nm and a shoulder at 320 nm (Table-1).

Table-1. The spectral characteristics of cocodiethanolamide depend on pH.

pH of the solution	wavelength, nm	$\epsilon_{exp.}, l \cdot mol^{-1} \cdot cm^{-1}$
4	200	71000
	255-260 (shoulder)	14000
	315-320 (shoulder)	7000
6	200	11000
	255-260 (shoulder)	2500
	320-325 (shoulder)	1400
8	200	64000
	260	6500
	320-325 (shoulder)	2700
10	210	130000
	235-240 (shoulder)	46000
	255-260 (shoulder)	29000
	320	15000

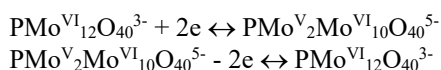
The obtained UV spectral characteristics of cocamide solutions show the presence of a characteristic absorption maximum at a wavelength of 200-210 nm of high intensity and the presence of a low-intensity shoulder at 315-325 nm, regardless of the acidity of the solution under study. Also, in alkaline and slightly acidic solutions, the presence of an absorption maximum or shoulder of average intensity is observed at 255-260 nm, and pH 10 an



additional absorption shoulder of average intensity appears at 235-240 nm.

Polyoxometalates are also characterized by intense absorption in the UV region of the spectrum. Figure-3 shows the UV absorption spectra of the oxidized (yellow) and reduced (blue) forms of polyoxomolybdate. Polyoxometalate ions are capable of partial reversible reduction, while several ligand atoms reduce the oxidation state by 1-2 units [9-10]. As a result of this reduction, mixed-valent compounds with intense color are formed (heteropoly blue).

The following reaction is typical for molybdenum polyoxometalates:



In this case, the structure of the polyoxometalate and the UV spectra should not change.

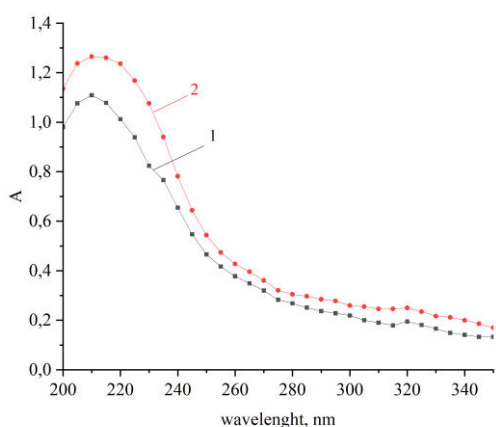


Figure-3. UV absorption spectrum of various polyoxometalates: $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (1) and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (2).

High values of the molar absorption coefficient in this region are due to charge transfers ($\delta-\delta^*$). They are attributed to the bands of electron transfer from filled molecular orbitals, which are formed mainly by p-orbitals of Oxygen to vacant orbitals localized on metal atoms $\text{O} \rightarrow \text{Me}$. The band in the region of 200-220 nm is the most high-energy ($\epsilon_{\text{exp.}} \sim 11000-12000$) related to charge transfer along the terminal $\text{Me} - \text{O}_t$ Bonds, an absorption band of medium intensity at 230-250 nm ($\epsilon_{\text{exp.}} \sim 8000$) and a low-energy absorption band at 330 nm ($\epsilon_{\text{exp.}} \sim 2000$) characterize charge transfer in linear and angular bridge bonds $\text{Me} \leftarrow \text{O} \rightarrow \text{Me}$.

To study the effect of solution acidity on the interaction reaction of the CDEA complex with polyoxomolybdate ions and to determine rational reaction conditions, the spectral characteristics of supramolecular complexes were recorded depending on pH in the UV region of the spectrum (Figures 4-5).

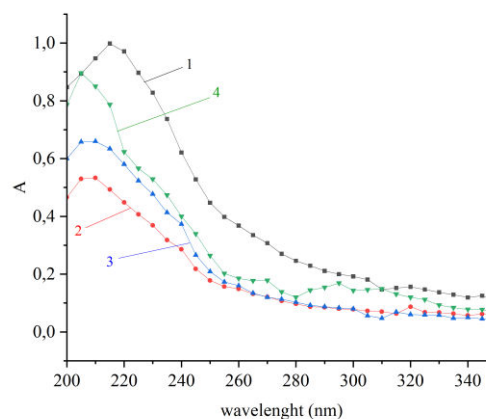


Figure-4. UV absorption spectrum of the supramolecular complex CDEA-POM($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) depending on pH: pH=4 (1), pH=6 (2), pH=8 (3), pH=10 (4).

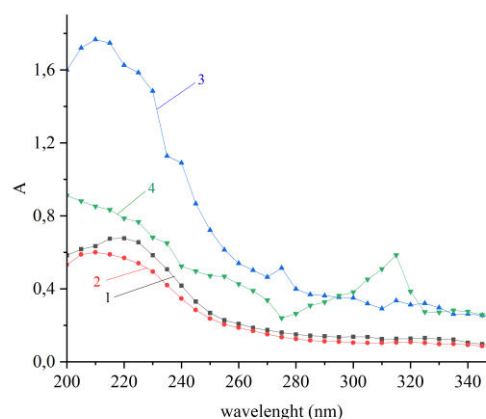


Figure-5. UV absorption spectrum of the supramolecular complex CDEA-POM($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) depending on pH: pH=4 (1), pH=6 (2), pH=8 (3), pH=10 (4).

Tables 2 and 3 present the obtained experimental data on the UV absorption spectra of catamine AB, polyoxometalates, and the resulting supramolecular complexes depending on pH.



Table-2. Spectral characteristics of supramolecular complexes based on $H_3PMo_{12}O_{40}$ depending on pH.

pH	Substance	wavelength, nm	$\epsilon_{exp}, l \cdot mol^{-1} \cdot cm^{-1}$
-	$H_3PMo_{12}O_{40}$	215	11000
		230-235 (shoulder)	8000
		320	2000
4	CDEA	200	71000
		255-260 (shoulder)	14000
		315-320 (shoulder)	7000
	CDEA- $H_3PMo_{12}O_{40}$	215	100000
		320	16000
6	CDEA	200	11000
		255-260 (shoulder)	2500
		320-325 (shoulder)	1400
	CDEA- $H_3PMo_{12}O_{40}$	205-210	53000
		235-240 (shoulder)	29000
		255-260 (shoulder)	1600
		320	9000
8	CDEA	200	64000
		260	6500
		320-325 (shoulder)	2700
	CDEA- $H_3PMo_{12}O_{40}$	205-210 (shoulder)	66000
		235-240 (shoulder)	37000
		255-260 (shoulder)	17000
		315	7000
10	CDEA	210	130000
		235-240 (shoulder)	46000
		255-260 (shoulder)	29000
		320	15000
	CDEA- $H_3PMo_{12}O_{40}$	205	90000
		225-230 (shoulder)	57000
		260-270 (shoulder)	18000
		295	17000

Supramolecular complexes of CDEA and the oxidized form of polyoxomolybdate (VI) contain an absorption maximum or high-intensity shoulder at 205-215 nm, two moderate-intensity shoulders at 225-245 nm and 255-270 nm, and a medium-intensity absorption maximum at 315-320 nm.

As can be seen from the presented data, as a result of the interaction of CDEA with POM_{ox} , at pH = 4-8, an increase in optical density is observed while maintaining the absorption maxima of the starting substances, which indicates the ion-associative nature of the bond in the resulting supramolecular compound. At pH 10, such an

increase in absorption is not observed, which can be explained by the decomposition of POM in a highly alkaline environment [9-10]:



At pH=4, only two absorption maxima are observed at 215 and 320 nm, which can be explained by the lack of interaction between the components in an acidic environment, since CDEA exists in dissolved form only in a neutral and alkaline environment (depending on the



concentration), and upon acidification it precipitates in sediment.

Table-3. Spectral characteristics of supramolecular complexes based on $H_5PMo_{12}O_{40}$ depending on pH.

pH	Substance	wavelength, nm	$\epsilon_{exp.}, l \cdot mol^{-1} \cdot cm^{-1}$
-	$H_5PMo_{12}O_{40}$	210-215 (shoulder)	12500
		320	2500
4	CDEA	200	71000
		255-260 (shoulder)	14000
		315-320 (shoulder)	7000
	CDEA- $H_5PMo_{12}O_{40}$	215-220	68000
6	CDEA	200	11000
		255-260 (shoulder)	2500
		320-325 (shoulder)	1400
	CDEA- $H_5PMo_{12}O_{40}$	210	60000
8	CDEA	200	64000
		260	6500
		320-325 (shoulder)	2700
	CDEA- $H_5PMo_{12}O_{40}$	210	176000
235-240		110000	
275		52000	
		315	34000
10	CDEA	210	130000
		235-240 (shoulder)	46000
		255-260 (shoulder)	29000
		320	15000
	CDEA- $H_5PMo_{12}O_{40}$	200-205	90000
		240-245	52000
315		58000	

Supramolecular complexes of CDEA and the reduced form of polyoxomolybdate (V, VI) contain high-intensity absorption maximum at 200-220 nm, a medium-intensity shoulder at 235-245 nm, and a medium-intensity absorption maximum at 315 nm.

As can be seen from the presented data, as a result of the interaction of CDEA with POM at pH = 8-10, an increase in optical density is observed while maintaining the absorption maxima of the starting substances, which indicates the ion-associative nature of the bond in the resulting supramolecular compounds. At pH = 4 and pH = 6, only the main absorption maximum at 210 nm is observed.

CONCLUSIONS

a) The effect of solution acidity on the properties of diethanolamine cocamide was studied using UV

spectroscopy. The pH of the solution does not significantly affect the absorption spectra in the range of 4-8, but at pH = 10 the structure of the substance changes and an additional chromophore group appears.

- b) The reaction of the synthesis of the supramolecular complex of cocamide DEA with various molybdenum polyoxometalates was studied using a spectroscopic method, depending on the acidity of the solution. The associative nature of the interaction of the reacting compounds was confirmed.
- c) When using the oxidized form of POM, the rational pH of the reaction for the formation of the supramolecular complex KDEA-POM is in the range of 4-8, and for the



reduced form POM rational acidity of the working solution is in the range of 8-10.

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