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SPECTROSCOPIC RESEARCHING OF THE INTERACTION REACTION OF COCAMIDOPROPYLBETAINE WITH 12-MOLYBDOPHOSPHATE HETEROPOLYACID

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ABSTRACT

The influence of the acidity of the working solution on the properties of the ampholytic surface-active substance of cocamidopropylbetaine is researched by a spectroscopic method in the UV-range. The possibility of the reaction behavior between the organic cation of cocamidopropylbetaine and the anion of 12-molybdophosphate heteropolyacid was investigated, and the nature of the bond in the obtained ionic associates was determined. The ionic nature of the bond in the product of the reaction of cocamidopropylbetaine and 12-molybdophosphate heteropoly acid was also confirmed by IR-spectroscopy. The composition of the complex and the ratio of the components of the reaction was determined spectrophotometrically at a wavelength of 248 nm by saturation method. The results of these researches can be used to develop methods for the determination of cocamidopropylbetaine in various industrial objects by the ionometric method using potentiometric sensors sensitive to this substance.

Keywords: 12-molybdophosphate heteropolyacid, cocamidopropilbetain, lauramidopropilbetain, surface-active substance, UV spectrophotometry, IR spectroscopy.

INTRODUCTION

Cocamidopropylbetaine(lauramidopropylbetaine) is an ampholytic surfactant derived from betaine. This compound forms dipole ions in solution and can exist as a zwitterion in a wide range of acidity. The isoelectric point for lauramidopropyl betaine is observed at pH = 5.4 [1].

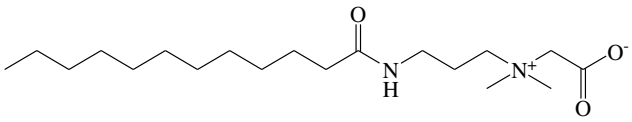

Figure-1. Cocamidopropylbetaine structural formula.

Lauramidopropylbetaine is used in the manufacture of detergents and cosmetics as a primary and auxiliary surfactant, foam stabilizer, thickener, conditioner and antistatic agent in hair products [2-6]. Cocamidopropylbetaine (CAPB) has a low irritant effect on the eyes and skin and can be used in cosmetics for children due to this property. [7-9]. The next methods can be used for the quantitative determination of cocamidopropylbetaine: liquid chromatography [10-11], a spectrophotometric method [12] potentiometric titration method with a glass electrode [13] and a titrimetric method based on the neutralization reaction [14]. The latter method is commonly used to establish the purity of industrial samples of cocamidopropylbetaine. According to previous studies [15-24], the development of ionometric methods for the quantitative determination of organic substances using potentiometric sensors is a promising direction in the development of alternative methods for determining the content of these substances in samples of various industrial products. The possibility of a chemical reaction between lauramidopropyl betaine and the heteropoly acid of the Keggin structure was previously investigated for this purpose. The nature of the bond in the obtained compounds was studied, and the optimal conditions for obtaining an ionic associate for the membrane of a potentiometric sensor were selected.

MATERIALS AND DEVICES

Spectrophotometric studies carried out with the spectrophotometer SF-46 (UV- spectra).
The following reagentsare used in the work:

- 12-molybdophosphate acid, $H_3PMo_{12}O_{40}x26H_2O$ (analytically pure);
- cocamidopropilbetaine,$C_{19}H_{38}N_2O_3$(analytically pure);
- sodium hydroxide (analytically pure);
- chloride acid (conc.) (analytically pure).

IR spectra were studied on a NICOLET IR-spectrometer (Impact-400) with a Fourier transform.

EXPERIMENTAL PART

The absorption spectra were recorded in the UV spectral range (200 - 330 nm) to study the effect of the acidity of the solution on the properties of cocamidopropilbetaine. The thickness of the cuvette with

the solution was 1.0 cm; distilled water was used as a comparison solution and solvent (Figures 2-3).

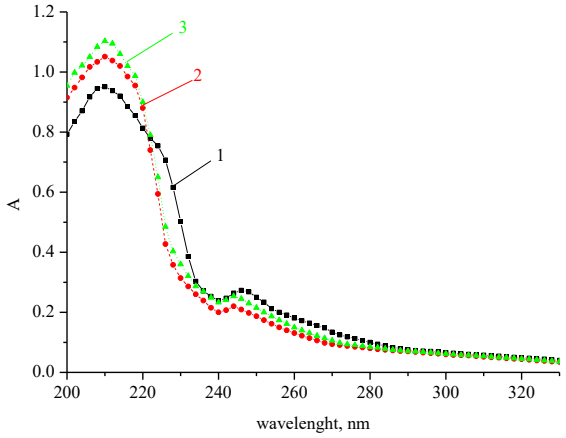

Figure-2. The UV absorption spectrum of CAPB solutions in the acidic pH range: pH = 1.0 (1), pH = 3.0 (2), pH = 5.0 (3).

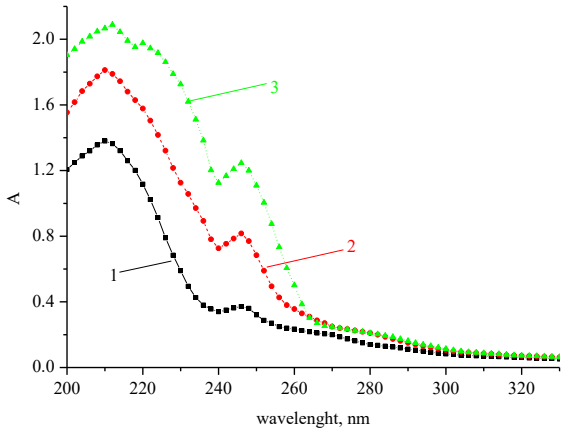

Figure-3. The UV absorption spectrum of CAPB solutions in the alkaline pH range: pH = 7.0 (1), pH = 9.0 (2), pH = 12.0 (3).

The UV-spectra of cocamidopropylbetaine solutions contain several characteristic absorption bands:

- the intense absorption band with a maximum at 210 - 220 nm corresponds to the presence of the - NH_2 chromophore group in the molecules of this substance and appears due to the presence of a free electron pair in the molecule of this substance on the Nitrogen atom ($n \rightarrow \sigma^*$ transition).
- the carbonyl group R – C = O – NH– also absorbs in the range 210 - 220 nm ($\pi \rightarrow \pi^*$ transition);
- a low-intensity absorption band with a maximum at 245 - 248 nm can be due to the presence of a carbonyl group in the molecule of this substance, which is attached to the quaternary atom of the Nitrogen of the carbonyl group.

Table-1 shows the characteristics of the UV absorption spectra of solutions of lauramidopropylbetaine depending on the acidity of the working solution.

Table-1. Characteristics of the UV absorption spectra of CAPB as a function of pH.

pH of the solution	λ_{max}, nm	$E_{exp.}$, l·mol^{-1}·cm^{-1}
1	210	950
	244 (shoulder)	260
3	210	1050
	245	220
5	210	1100
	245	250
7	210	1380
	246(shoulder)	370
9	210	1810
	246	820
12	212	2090
	220	1970
	246	1250

The absorption increases with an increase in the acidity of the solution of lauramidopropylbetaine. The additional absorption band appears at pH = 12.0 at 220 nm, which is explained by the presence of the conjugated carbonyl group R - CO - R in the molecule of this substance. This absorption band disappears due to the blocking of a free pair of electrons due to protonation in an acidic medium.

In order to study the possibility of obtaining an electrode-active substance for potentiometric sensor membranes sensitive to the substance under study, the spectral characteristics of the combination of lauramidopropyl betaine with 12-molybdophosphate heteropolyacid depending on the acidity of the working solution were studied (Figures 4-6).

The spectral manifestations of cocamidopropylbetaine, 12-molybdophosphate heteropoly acid and the product of their interaction depending on the pH of the solution are shown in Table-2.

Table-2. UV absorption spectra of the researched compounds.

pH of the solution	Substance	λ_{max}, nm	$E_{exp.}$, l·mol^{-1}·cm^{-1}
-	$H_3PMo_{12}O_{40}$ (MPhA)	215	60000
		235 (shoulder)	34000
		320	12000
3	CAPB	210	1050
		245	220
	CAPB-MPhA	212	110600
		235	31400
		248	23000
		320	15600
5	CAPB	212	1100
		245	250
	CAPB-MPhA	208	116000
		212	118000
		320	4000
9	CAPB	210	1810
		246	820
	CAPB-MPhA	208	315800
		220 (shoulder)	258800
		246	145800

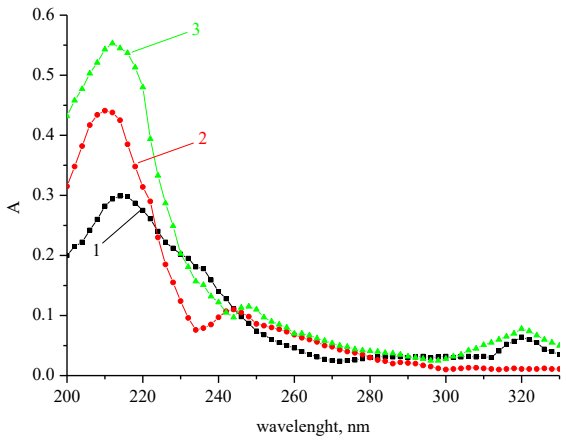

Figure-4. UV-spectral characteristics of the solutions at pH = 3.0: MPhA (1), CAPB (2), CAPB-MphA (3).

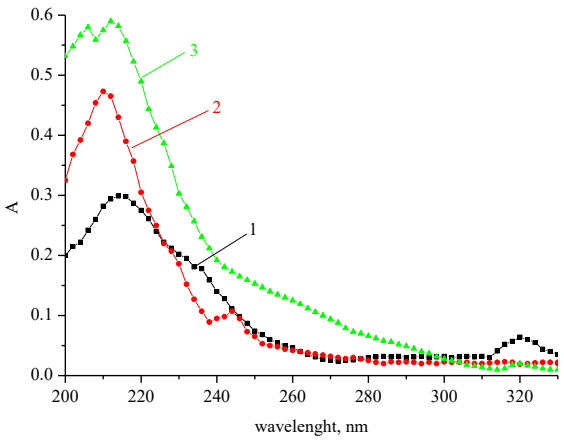

Figure-5. UV-spectral characteristics of the solutions at pH = 5.0: MPhA (1), CAPB (2), CAPB-MphA (3).

The next absorption maxima are characteristic of the UV spectrum of the 12-molybdophosphate heteropoly acid:

- the absorption band at 215 nm corresponds to the O = Me groups and appears due to the transfer of electrons from the orbitals of Oxygen atoms to a metal atom [26-27];

- absorption bands at 235 and 320 nm correspond to charge transfers along O - Me - O bridge bonds.

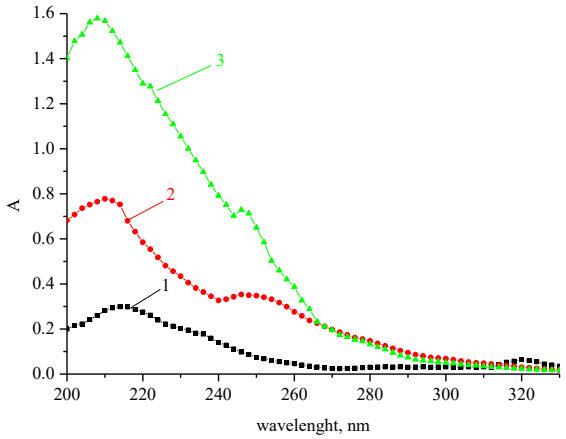

Figure-6. UV-spectral characteristics of the solutions at pH = 9.0: MPhA (1), CAPB (2), CAPB-MphA (3).

The reaction product of the interaction of the organic cation of cocamidopropylbetaine and the heteropolyanion of 12-molybdophosphate acid contains characteristic absorption bands of the starting compounds at pH = 3.0. The absorption bands of the heteropolyanion are not completely present in the spectra at pH = 5.0 and pH = 9.0. Therefore, in this case, we cannot speak of the formation of products with the ion-associative nature of the bond during the reaction. At pH = 3.0, the UV spectrum of the obtained compound contains absorption bands that are characteristic of both 12-molybdophosphate heteropolyacid and lauramidopropylbetaine, which indicates the invariance of the chromophore system during the interaction. Moreover, a deviation from the additivity law is also observed, which is confirmation of the ion-associative nature of the bond in the resulting compound.
The composition of the obtained ionic associate was determined by a saturation method at a wavelength λ = 248 nm (Figure-7). The aqueous solution of lauramidopropyl betaine with a concentration of $5.0 \cdot 10^{-4}$ M at pH =3.0 was saturated with an aqueous solution of 12-molybdophosphate heteropolyacid $H_3PMo_{12}O_{40}$ with a concentration of $5.0 \cdot 10^{-4}$ M according to the used method.

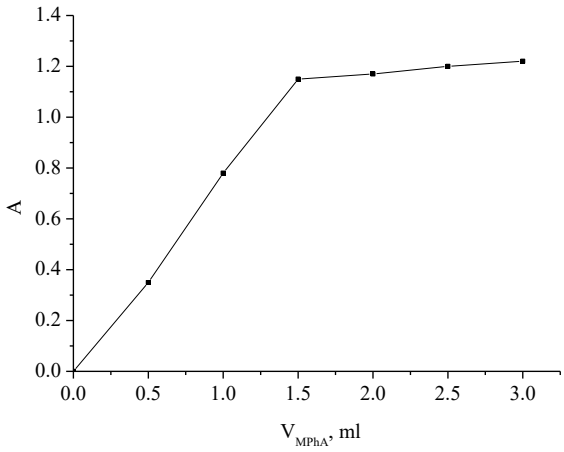

Figure-7. Saturation curve of the CAPBwithMphA.

The ratio of the reaction components is $[CAPB^+]$: $[PMo_{12}O_{40}^{3-}] = 3:2$ according to the results of the spectrophotometric determination. Therefore, the interaction of cocamidopropylbetaine with MPhA forms an ionic associate of the composition $(CAPB)_3(PMo_{12}O_{40})_2$.

IR spectroscopy in the range 4000 - 600 cm^{-1} was used In order to confirm the ion-associative nature of the interaction between the 12-molybdophosphate heteropoly acid and lauramidopropylbetaine, as well as to identify the resulting ion associate (Figure-8).

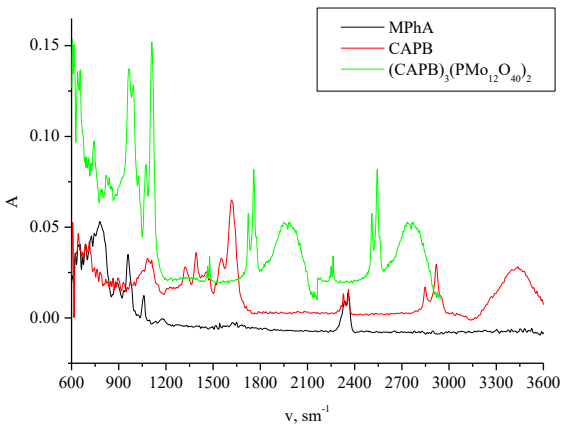

Figure-8. IR spectra of test substances.

Table-3. Assignment of absorption bands in the IR spectra of the studied compounds.

Substance	v, sm^{-1}							
	C-H	**C=O**	**C-N**	**N-H**	**N-C=O**	**P-O**	**Mo-O**	**Mo-O-Mo**
$H_3PMo_{12}O_{40}$	**-**	**-**	**-**	**-**	**-**	**1058**	**958**	**886 782**
CAPB	2926 2853 978 939 903 885 869 767 751 720	1626	1399 1328 1088	3340 1555 1469 854 823	1555	-	-	-
$(CAPB)_3(PMo_{12}O_{40})_2$	3305 2924 2853 799 717	1627	1397 1337 1087	3380 1551 1457 853 827	1551	1050	964	892 779

Thefollowingabsorptionfrequenciesarecharacteristicoftheirspectrumofthelauramidopropylbetainemolecule:

- absorption bands of valent and deformed vibrations of CH methyl and methylene groups in the ranges 3000 - 2840 sm^{-1}, 1475 - 1430 sm^{-1}, 1395 - 1365 sm^{-1}, 1250 - 800 sm^{-1}, 770 - 720 sm^{-1};
- valent bands of C-N groups in the range of 1400 - 1000 sm^{-1};
- fluctuation bands of N-H groups in the range of 3500 - 3100 sm^{-1};
- the absorption band of the C = O group at a frequency of 1626 cm^{-1};
- the absorption band of the group N-C = O at a frequency of 1555 sm^{-1}

The IR spectrum of a 12-molybdophosphate heteropoly acid contains characteristic absorption bands in the range of 1000 - 900 sm^{-1} (terminal multiple bonds Mo = O and tetrahedral PO_4 anions), absorption bands in the range of 900 - 700 sm^{-1} (bridging linear and angular bonds Mo - O - Mo) [26-27].

The IR spectrum of the reaction product of cocamidopropylbetaine with 12-molybdophosphate heteropoly acid retains the characteristic vibrational bands of Mo = O and Mo - O - Mo in the range of 1000 - 700 sm^{-1}, which indicates the preservation of the structure of MPhA. There are also absorption bands of bonds that are characteristic of lauramidopropyl betaine according to spectrum: C - N in the range of 1400 - 1000 sm^{-1}, C = O in the range of 1740 - 1630 sm^{-1} and N - C = O in the range of 1630 - 1510 sm^{-1}. The obtained data indicate the associative nature of the interaction between the surfactant and heteropolyanion.

4. CONCLUSIONS

a) The effect of the acidity of the working solution on the properties of cocamidopropylbetaine was investigated with UV spectrophotometry. This substance is characterized by absorption maxima at 210 - 220 nm and 245 - 248 nm. The absorption increases with increasing acidity of the test solution, and the additional absorption band appears at 220 nm at pH = 12.0 on the spectrum.

b) The effect of pH on the possibility of passing the interaction reaction between the organic cation of lauramidopropyl betaine and the anion of 12-molybdophosphate heteropoly acid has been researched. It was found that the optimal acidity of the test solution to obtain the product is pH = 3.0.

c) The ratio of the components in the reaction of cocamidopropylbetaine cation and heteropolyanion cation is 3:2 and the ionic associate of the composition $(CAPB)_3(PMo_{12}O_{40})_2$is formed were found using UV-spectrophotometric saturation.

d) The ion-associative nature of the bonds in the resulting product by the interaction of the organic cation of cocamidopropylbetaine with the heteropolyanion of 12-molybdophosphate heteropoly acid was confirmed with IR-spectroscopy.

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