

Dedicated to Professor Dr. ALEXANDRU T. BALABAN, member of the Roumanian Academy on the occasion of his 75th anniversary

SYNTHETIC MEMBRANES DERIVED FROM PYRIDINIUM SALTS WITH LONG ALKYL SUBSTITUENTS HAVING A TERMINAL FREE AMINO GROUP¹

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2,4,6-Trisubstituted pyrylium salts having either one or two linear α -alkyl side chains **1** reacts with ethylene diamine **2** affording the corresponding pyridinium salts with a free amino group **3a-3d**. All new amphiphiles were fully characterized by ¹H- and ¹³C-NMR (at 400 MHz for protons and 100 MHz for carbons), IR and elemental analysis. The preparation of the new compounds enabled us to examine the effects of the amphiphilic structure on the aggregation properties. Considering the dynamic light scattering (DLS) and UV spectroscopy measurements, the paper examines the surfactant properties of these pyridinium salts having a free amino group and explores the properties of the derived synthetic membranes. The reaction of these membranes with fluorescein is also reported.

INTRODUCTION

In a series of papers we have reported the synthesis of several pyridinium salts with long alkyl substituents in α or γ positions derived from the corresponding pyrylium salts.^{1, 8-15}

The first synthesis of pyrylium salts from various alkene precursors such alcohols or t-butyl / amyl halides under Friedel–Crafts conditions have been used with success in preparative organic chemistry.²⁻⁷

Prof. A.T. Balaban described the synthesis of 2,4,6-trimethyl-1-(para-alkylphenyl) pyridinium tetrafluoroborates with the n-alkyl group having 8 to 16 carbon atoms. Their surfactant properties were presented.⁶ These compounds were mentioned to be anticorrosive agents.⁷

The diacylation of olefins has been worked out extensively during the past years in our laboratory and the several substituted pyrylium salts with long alkyl substituents and derived pyridinium salts were prepared.⁸⁻¹⁵

This article is concerned with special pyridinium salts **3a-3d** having the functional group as a terminal amino group. The most elegant route² was used to prepare this new class of compounds that contains each of the desired function:

- hydrophobic character;
- hydrophilic character;

¹ This is contribution no. 10 in the series “Pyrylium Salts with Long Alkyl Substituents”. For some previous papers in this series see ref. ^{1, 8-15}.

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– ability for crosslinking by the terminal amino group.

Current ways of measuring critical micelle concentration (CMC) use the very common techniques in physical chemistry laboratories which include UV-VIS spectroscopy, surface tension change, and electro-conductivity change of the surfactant solutions.¹⁶

UV-VIS spectroscopy applied to the determination of the CMC of surfactants is a convenient method with good reproducibility. Red-shift of a particular peak in the UV-VIS spectrum could be observed when surfactant micelles are formed at the CMC. In addition, the results from the UV-VIS data are useful in controlling the micellar reactors and in studying the molecular clustering phenomena.¹⁷⁻¹⁹

We determined the critical micellar concentration (CMC) of the N-ethyleneamino-pyridinium salts with different long chain substituents **3a-3d**, using spectrophotometry methods in the UV-VIS region of the spectrum at 20 °C. We found the dependence of the CMC on the number of the carbon in the alkyl side substituent chains.

Several biosurfactants have high surface activities and low critical micellar concentration (CMC) and are, therefore, promising substitutes for synthetic surfactants.²⁰ Pyridinium salts with long alkyl substituents are ideal compounds for practical applications as surfactants and in non-viral gene delivery^{21,22} due to their biocompatibility and low CMC.

In a previous paper,⁸ the preparation of novel artificial membranes derived from various pyridinium salts was presented. We also examined the synthesis of N-triethyl-triaminopyridium perchlorates and derived artificial membranes (data are given in the supplementary material).²³

The present paper describes the preparation of a new artificial membrane having ethyleneamino terminal group. The influence of the new free amino group on the membrane stability, the reaction of this with fluorescein and dynamic light scattering (DLS) experiments are presented.

RESULTS AND DISCUSSION

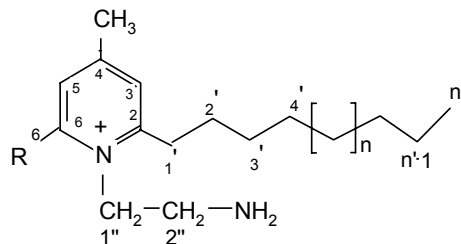
Materials and methods

In previous papers^{1,8-15} we reported the synthesis and the chromatographic separation of the complex acylation mixture ending in the isolation of the pyrylium salts in pure state. This procedure was successfully used for the pyrylium salts **1**.

By reaction between salts **1** with ethylene diamine (CH₂NH₂)₂, the pyridinium salts **3a-3d** were obtained. The reaction mixture contains pyridinium and bis-pyridinium salts. The conditions and the purification procedures are given in the Experimental part (Scheme 1).

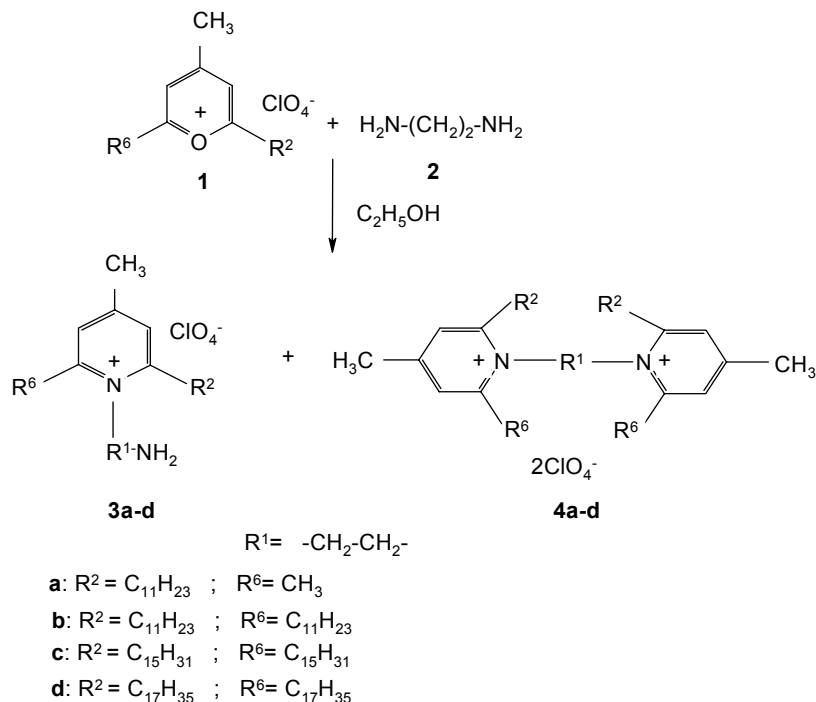
The ¹H and ¹³C-NMR chemical shifts of pyrylium salts **3a-3d** were in agreement with the previously reported NMR data on the 2,4,6-trisubstituted homologs.^{1, 8-15}

The atom numbering for the NMR assignments is presented in Fig. 1:



3a	n = 4	R ⁶ = CH ₃
3b	n = 4	R ⁶ = C ₁₁ H ₂₃
3c	n = 8	R ⁶ = C ₁₅ H ₃₁
3d	n = 10	R ⁶ = C ₁₇ H ₃₅

Fig. 1 – The atom numbering for NMR assignments.



Scheme 1 – Conversion of pyrylium salts into N-ethylene-amino pyridinium salts 3a- 3d.

Table 1 presents the 1H and ^{13}C -NMR chemical shifts for these new compounds.

Table 1

1H and ^{13}C -NMR for compounds 3a-3d

Cpd.	1H and ^{13}C chemical shifts δ (ppm) in $CDCl_3$															
	Aromatic ring					Aliphatic substituents										
	2C	3C*	4C	5C*	6C	4CH ₃	6CH ₃	1'CH ₂	2'CH ₂	3'CH ₂	4'	(n ² -2)	(n ² -1)	n'	1''	2''
3a	-/ 158.13	7.48/ 127.60	-/ 159.77	7.62/ 129.96	-/ 155.54	2.57/ 21.90	2.74/ 21.82	3.07/ 33.92	1.73/ 28.28	1.40/-	1.26- 1.38/-	-/ 31.91	-/ 22.62	0.88/ 14.08	4.85/ 49.40	3.5/ 37.77
3b	-/ 157.98	7.45/ 126.75	-/ 158.43	-/ -	-/ -	2.58/ 21.99	-/ -	3.12/ 34.01	1.75/ 27.88	1.46/-	1.26- 1.40/-	-/ 31.37	-/ 22.67	0.88/ 14.08	4.60/ 48.18	3.60/ 38.65
3c	-/ 157.95	7.54/ 127.79	-/ 158.53	-/ -	-/ -	2.58/ 22.68	-/ -	3.11/ 34.02	1.71/ 28.93	1.47/-	1.26- 1.40/-	-/ 31.92	-/ 22.98	0.89/ 14.04	4.53/ 48.22	3.58/ 38.74
3d	-/ 157.99	7.48/ 127.80	-/ 158.52	-/ -	-/ -	2.58/ 22.69	-/ -	3.12/ 34.02	1.75/ 28.93	1.48/-	1.26- 1.40/-	-/ 31.93	-/ 22.98	0.88/ 14.04	4.58/ 48.23	3.64/ 38.75

*assignment based on H-C 2D spectra

The assignment of the proton signal is in all cases straightforward. When the signals were ascertained, 2D techniques were used.

The 2,4,6-trialkylpyridinium salt moiety is a very useful probe for measuring the ring current of aromatics as an internal reference. In the carbon spectra five atoms of the long alkyl side chains have signals unambiguously assigned from inverse detection H-C HMQC and H-C long range correlation (HMBC) with z gradients spectra.

Surfactant properties

The amphiphiles **3a-3d** dissolved in water or other polar solvents tend to associate and to form micelles. In the resulting micelles the long alkyl side chains (the hydrophobic part) form the micellar core and the N-ethyleneamino group (the hydrophilic part), soluble in polar solvent, form a shell around the core.

The UV-VIS spectra of the monomeric state **3a-3d** in the range 200-400 nm are characterized by two bands whose intensities and positions are solvent dependent. Upon aggregation the absorbance of these

bands decrease in magnitude. The UV-VIS spectra of these in compounds ethanolic solution were presented in the Experimental part.

In order to obtain the diagrams absorbances *vs* concentration for CMC determination, the mixtures **3a-3d** / ethanol were prepared and let to stand at 20 °C for one day and by measuring absorbance as a function of amphiphiles concentration, one can estimate their CMC from the intercept of two straight lines. A typical plot that was used for the determination of the CMC of **3a** (λ , nm = 270.97) is shown in Fig. 2. By using such methods the CMC values for **3b-3d** are estimated to be 5.33 (λ , nm = 235.95), 3.50 (λ , nm = 235.95) and 2.98 (λ , nm = 235.95) mM $\times 10^{-3}$. The results were similar to that observed by T. Kunitake *et al.*²⁴ for azobenzene-containing amphiphiles which absorb at shorter wavelengths upon aggregation.

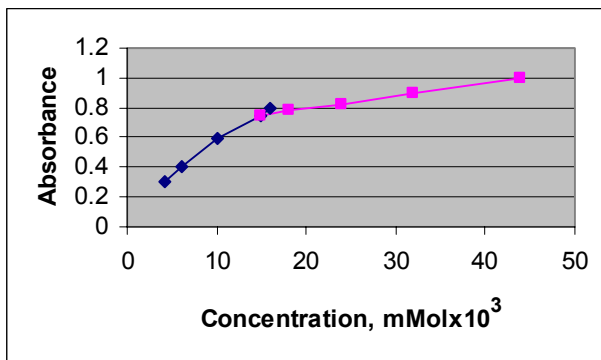


Fig. 2 – Concentration dependence of absorbance for **3a**.

It is found that the CMC decreases with the increasing length of the hydrophobic alkyl group.²⁵ Fig. 3 shows the diagram CMC *vs* the number of carbon atoms of the alkyl side chains for compounds **3a-3d** and according to the well-known data, a drastic decrease of the CMC was observed.

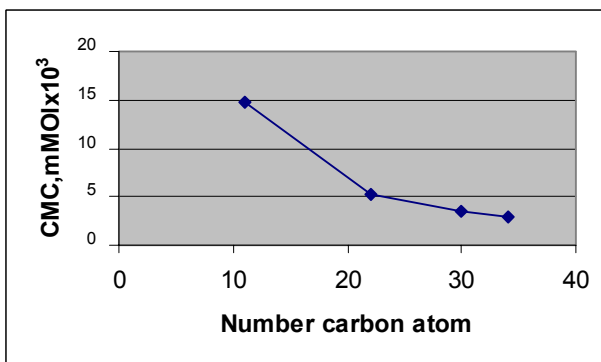


Fig. 3 – Plot of CMC as a function of the length of the hydrophobic alkyl side chains.

General procedure for the preparation and characterization of membranes. Reaction with fluorescein

The experimental protocol describing the conditions to obtain the new synthetic membranes was given in the Experimental Part. Membranes derived from pyridinium salts **3a-3d** were prepared by Langford Somatic, T 175 bath-type sonicator; a similar procedure to that described previously was employed.⁸

They were studied by optical microscopy (OM), phase separation (membrane stability), dynamic light scattering (DLS) and differential scanning calorimetry (DSC)²⁶ in order to learn to control the self-assembly process.

In previous papers⁸ we presented the relationships between the cationic amphiphiles and their aggregates and the influence of the cationic amphiphile chemical structures on the membrane stability (phase separation) and the aggregate morphologies which are observed by optical microscopy (OM). For the **3a-3d** complex structures with variable morphologies and a dynamic process of self-assembly were observed. The time interval from sonication until phase separation was over 60 days.

The reaction with fluorescein was employed according to the method optimized by T. Kunitake *et al.*²⁷ In all cases the fluorescence intensity is a direct measure of the amount of the reacted amine or the permeation property of the surfactant vesicle. Fig. 4 shows the reaction of fluorescein with amine-aggregates derived from the pyridinium salts **3a-3d** with the different long alkyl substituents. Depending on the structure of the amphiphiles, variable times for the fluorescein reaction and different amino groups located at the outer surface or into the inner-surface of the double-walled vesicles were obtained.

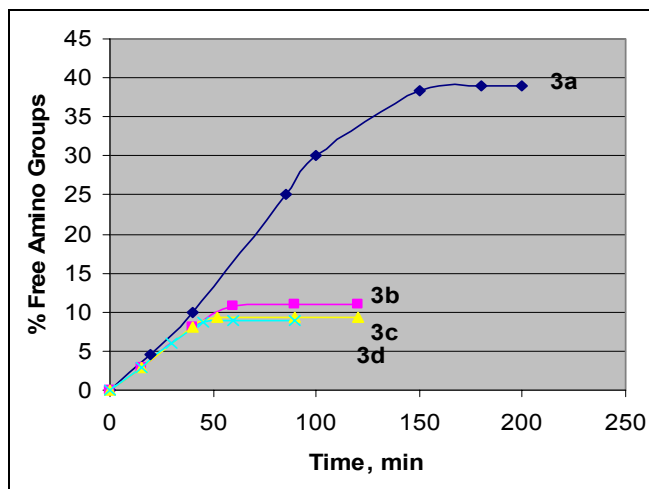


Fig. 4 – Reaction with fluorescein.

Dynamic light scattering (DLS) experiments

The Gaussian distribution to the dimensions of a species existing in aqueous solutions containing different concentrations of **3a-3d** is very wide. The effect of a new nonpolar chain length (**3b-3d**) on the diameter values indicates that the flexible chain makes a significant contribution to aggregation. Fig. 5 presents the variation of diameter in time, for **3a** and **3b**. The decrease of the carbon atoms number between 11 to 22 produces an increase of diameters which suggests two distinct modes of aggregation, a different solvation and a preferential hydrogen bond.

The formation of aggregates with considerably dimensions was obtained for **3a** and put into evidence by Nicomp Analysis Distribution (NAD). So, NAD analysis of 3.2 mM (CA, concentration of amphiphile) and 1.79×10^{-5} M (concentration DLS sample) aqueous solution of **3a** (Table 2) at 20 °C shows a maximum diameter at 1693.7 nm and a minimum of 239.1 nm. For **3b-3d** the size of the aggregates increases and different distributions were obtained.

Table 2

DLS results for **3a-3d** aqueous solutions at 20 °C

Cpd.	CA mM×10 ³	Conc. DLS M×10 ⁵	Time min / sec	Aggregate	
				d, nm	%
3a	3.20	1.79	19/23	239.1	10.0
				1693.7	90.0
3b	3.20	1.81	14/47	77.8	35.0
				698.8	65.0
3c	3.19	1.80	12/53	65.4	40.0
				650.9	60.0
3d	3.20	1.81	12/22	58.9	42.9
				630.4	57.1

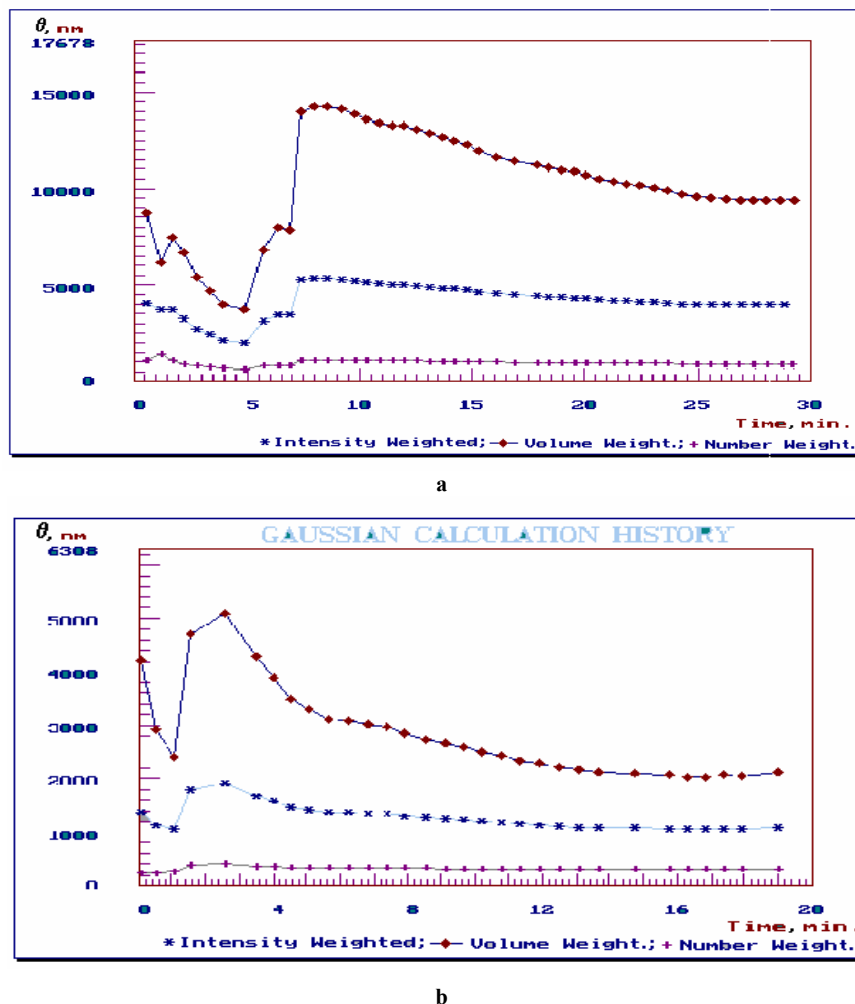


Fig. 5 – The Gaussian distributions for **3a** (a) and **3b** (b).

The variation of diameter in time for **3a**, put into evidence by NAD, is presented in Fig. 6. In the first and second steps two aggregates with very large diameters and distributions were found. These aggregates are split into three smaller species with different diameters and distributions. By the self-assembly of smaller aggregates ($d = 98$ nm) and the breaking of large aggregates ($d = 43.000$ nm), two types of aggregates were obtained. According to the Gaussian distribution, the system was stable. At the last time, the NAD distribution was bi-modal. The DLS results establish that spontaneous formation of stable membranes derived from **3a-3d** is obtained. The mode of the molecular orientation and distinct modes of aggregation of the amino amphiphiles in the corresponding membranes were reflected by the different process of self-assembly and the size of aggregates.

EXPERIMENTAL PART

The NMR spectra were recorded with a BRUKER AVANCE DRX 400 instrument, equipped with a 5 mm inverse detection multinuclear probe head and field gradients on the z axis, operating at 400 MHz for 1H and at 100 MHz for ^{13}C nuclei. The COSY45, HMQC and HMBC spectra were recorded with standard Bruker parameters in the versions employing pulsed field gradients. All spectra were recorded in deuterated chloroform, and the chemical shifts were reported as δ values referenced to TMS as internal standard. The reaction products were initially checked using a Varian EM 360 NMR spectrometer operating at 60 MHz for 1H -nuclei. Infrared spectra were run on Zeiss UR 20 instruments. The UV-VIS spectra were recorded with a GBC type 918 instrument in 1 cm cuvettes. Melting points were measured in open capillary tubes (for the low melting compounds) or on a hot-stage melting points apparatus (equipped with a polarizer to check for nematic properties). The OM was performed with a microscope NIKON AFX-DX equipped with a digital camera. The dynamic light scattering (DLS) experiments were carried out using a NICOMP 370 equipment.

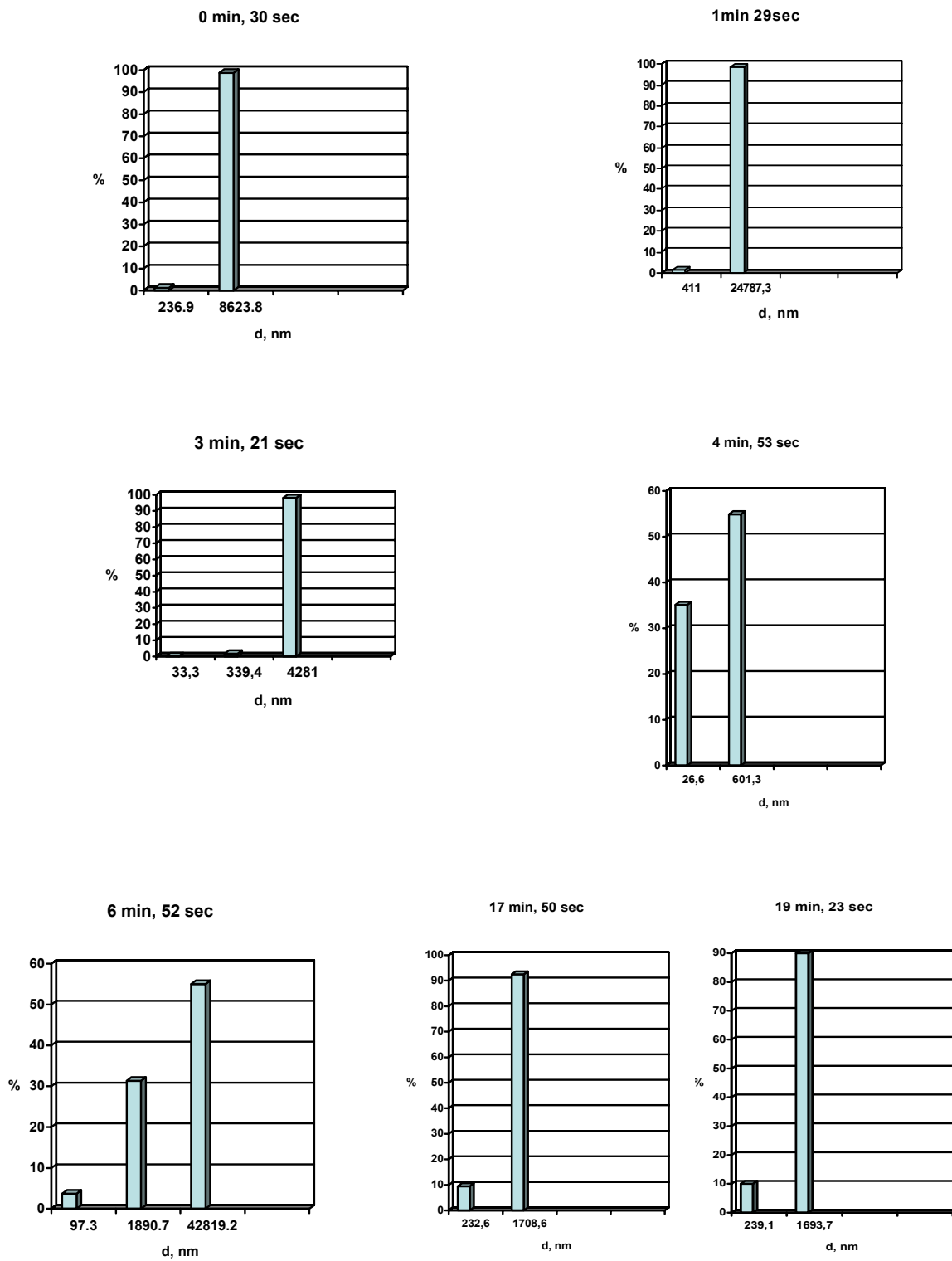


Fig. 6 – NAD results for 3a.

Conversion of pyrylium salts into N-ethylene-amino -pyridinium salts 3a- 3d

To the solution of pyrylium salt **1** in ethanol an excess of ethylenediamine **2** (40% in ethanol) was added (1:5 –1:10 molar ratio); a deep-red colour developed instantly. The mixture was heated at a gentle reflux of the solvent for 3-5 hours when the colour of the solution turned into cognac. The reaction mixture contains pyridinium and bis-pyridinium salts. After cooling the pyridinium salts were separated by thin layer chromatography (silica gel Merck type 60G, solvents ethyl acetate : methanol = 7:2 for **3a**, chloroform :methanol=1:1 for **3b** and hexane : acetic acid : ethyl acetate = 2 : 5 : 3 for **3c** and **3d**). The pyridinium salts **3a** and **3b** crystallized spontaneously, after storing for one hour in the refrigerator. Recrystallization from *i*-propanol gave colorless crystals with m.p.=103-103.5°C (**3a**) and with m.p.= 77-78°C (**3b**), respectively. For **3c** and **3d**, after solvents evaporation, waxy oils which crystallized in refrigerator were obtained (m.p.=20-22 °C for **3c** and m.p.=24-25 °C for **3d**).

The yields in **3a-3d** were 55%, 68%, 70% and 44%, respectively.

IR (CCl₄), cm⁻¹: 1100s, 1280mw, 1570w, 1635w, 2860m, 2930mw, 3580w, for **3a**.

IR (CCl₄), cm⁻¹: 1100s, 1280w, 1480mw, 1570w, 1635mw, 2860m, 2930mw, 3580w, for **3b**.

UV (EtOH), λ_{max} (nm): 224.95 and 270.97 for **3a**; 235.95 and 270.47 for **3b**; 235.95 and 270.45 for **3c**; 235.95 and 274.72 for **3d**.

The IR spectra for perchlorates **3c** and **3d** was in full agreement with the data presented for compounds **3b**.

3a C₂₀H₃₇N₂ClO₄ Calcd.: N 6.92%; found: N 6.89%.

3b C₃₀H₅₇N₂ClO₄ Calcd.: N 5.14%; found: N 5.25%.

3c C₃₈H₇₃N₂ClO₄ Calcd.: N 4.26%; found: N 4.30%.

3d C₄₂H₈₁N₂ClO₄ Calcd.: N 3.93%; found: N 3.90%.

Surfactant properties

In order to obtain the diagrams absorbances vs concentration for CMC determination, the mixtures **3a-3d** / ethanol were prepared and let to stand at 20 °C for one day. The UV-VIS spectra were recorded with a GBC type 918 instrument in 1 cm cuvettes.

Evaluation of absorption at a fixed wavelength and temperature and various concentrations of amphiphiles showed that the experimental points which intersect at the CMC value lie on two lines.

General procedure for the preparation of membranes

In all cases, given amounts (3.2 mM) of pyridinium salts **3a-3d** were first suspended and then sonicated in distilled water in a cleaning bath (Langford Sonomatic, T175) having the frequency of 33 kHz, using a 50 mL Erlenmeyer flask with a bottom area of 20 cm². Sonication times in the ultrasonic cleaning bath were 30 min for all compounds and the concentration was of the order of 3.2 mM. The obtained solutions which were either emulsions or (micro)dispersions were stored in closed vessels until analysis.

Reaction with fluorescein

An amine vesicle solution (5 mL) was mixed with a given amount of fluorescein in acetone (1%), at 20 °C. The reaction mixture was maintained with stirring at room temperature for 20-40 min. A 200 µL aliquot was added to 1mL ethanol and the fluorescence intensity at 460 nm was determined.

The fluorescein reaction was finished when an excess of fluorescein was observed. For the last aliquot, for all experiments, the modification of fluorescence intensity after 24 hours was not observed.

Dynamic light scattering (DLS)

The dynamic light scattering (DLS) experiments were carried out using a NICOMP 370 equipment. The scattering data were processed with two types of distributions: a Gaussian or a multimodal distribution referred to as Nicomp Analysis Distribution (NAD).

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