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AGGREGATION PROPERTIES OF CATIONIC GEMINI SURFACTANTS IN AQUEOUS SOLUTION[#]

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New cationic gemini surfactants bearing two hydrogen methanesulphonate groups and two long-chain alkyl groups (octyl, dodecyl or hexadecyl) were prepared in good yields by the reaction of N,N'-bis-alkyl,N,N'-bis(3-aminopropyl)ethylenediamine with methanesulphonic acid. All of these gemini salts showed good water solubility. Their aggregation ability in water has been determined by steady-state fluorescence spectroscopy. Furthermore, the micellar properties for the concentration near above the cmc have been characterized by the aggregation number, N_{agg}. The presence of the dimeric segments in the surfactant molecule is found to be in charge of their unusual physicochemical behavior. They are very efficient at adsorbing at the free surface and at forming micelles in water. Accordingly, both the micelle-forming property, and the ability to lower the surface tension increased with the increase in the length of the hydrophobic chain. The studied surfactants were found to form stable and reproducible n-tetradecane emulsions, for which the multimodal size distribution, effective diameter and zeta potential in the system: n-tetradecane/water/surfactant IVa-c have been determined.

Key words: dimeric surfactants, emulsions, surface activity, micelle aggregation number, steady-state fluorescence, PCS

INTRODUCTION

Surfactants with two hydrophilic and two hydrophobic groups in the molecule, called „gemini" surfactants (or „dimeric"), have evoked considerable interest (Menger et. al 2000, Oliviero et. al 2002, Zana et. al 1993, Rosen 1993, Mathias et. al 2001, Diamant et. al 1994, Camesano et. al 2000, Karaboni et. al 1994, Song et. al 1996) since it became evident that these surfactants appear to be superior to the corresponding conventional monomeric surfactants (i.e., with one hydrophilic and one hydrophobic group in the structure). Dimeric surfactants with a great variety of structures and differing in the nature of the head groups and spacer have been reported

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[#] This paper is dedicated to prof. A. Pomianowski on the occasion of his 80th birthday

(Menger et.al 2000, Oliviero et. al 2002, Diamant et. al 1994, Tatsumi et. al 2001, Manne et. al 1997, Knaebel et. al 2000, Wilk et. al in press, Paddon-Jones 2001). They reveal a greater tendency to absorb at the surface relative to their tendency to form micelles (Wilk et. al in press, Rosen et. al 1986). In the present contribution we describe first the interfacial and aggregation properties of a new series of cationic gemini surfactants which structures and the preparation route are shown in Table 1. In the second step of our studies we have examined the stability and formation of emulsions by surfactants IV a-c and n-tetradecane, used as the oil phase. Using the ZetaPlus instrument the effective diameter of microdroplets, sign and magnitude of zeta potential were acquired.

EXPERIMENTAL PROCEDURES

MATERIALS

The cationic gemini surfactants IV a-c were synthesized by the reaction of N,N’-bis-alkyl,N,N’-bis(3-aminopropyl)ethylenediamine (III) with methane-sulphonic acid (MsOH) in methanol. Preparation of III was carried out according to the method previously developed for the gemini sugar surfactants (Wilk et. al in press) and shown in Table 1, in which further intermediate compounds are indicated i.e.,N,N’-bis(3-nitropropyl)ethylenediamine(I),N,N’-bisalkyl(3-nitropropyl)ethylene-diamine(II). Purification of IVa-c was performed by a repeated crystallization from methanol/acetonitrile mixtures. Their purity and established structure were ascertained by electrospray ionization (ESI) mass spectrometry and elemental CHN analyses (Table 2). The ESI spectra were obtained with a Finnigan TSQ-700 mass spectrometer and the latter – a Perkin-Elmer CHN Analyser. 6-Propionyl-2-(dimethyl-amino)naphthalene (PRODAN) was purchased from Molecular Probes, Inc. (Eubene, Or 97402), tris(2,2`bipirydyl)rythenium(II) chloride hexahydrate ($Ru(bpy)_3^{2+}$) and 9,10-dimethylanthracene (9,10-diMeA) – from Aldrich Chemical Co. (Milwaukee, WI).Water of specific resistance at least 18.2 MΩcm was obtained by passing doubly distilled water through Millipore-MilliQ purification system.

METHODS

Air-water solution tension were measured with an accuracy of 0.01 mNm^{-1} at 25 ^{o}C ($\pm 0.1^{o}C$) by the duNuoy method using a Kruss K12 processor tensiometer. The absence in the γ=f(log c) curved minimum near the critical micelle concentration (cmc) is direct evidence for the purity of the studied surfactants. The cmc was taken as the concentration at the point of intersection of the two linear portions of the γ=f(log c) plots (Figure 1). The steady-state emission fluorescence spectra were recorded on an IBH 5000U spectrometer, used as a single-photon sensitive steady-state fluorimeter by means of an additional Model 5000U-06 steady-state accessory with xenon lamp. Emission and excitation slits were fixed at 16 nm. Measurements were performed in a thermostated cuvette holder at 25±0.5 °C. The cmc values of IVa-c were determined by means of the method previously described by Wong et al. (1999).

Table. 1. Structures and the preparation of cationic gemini surfactants

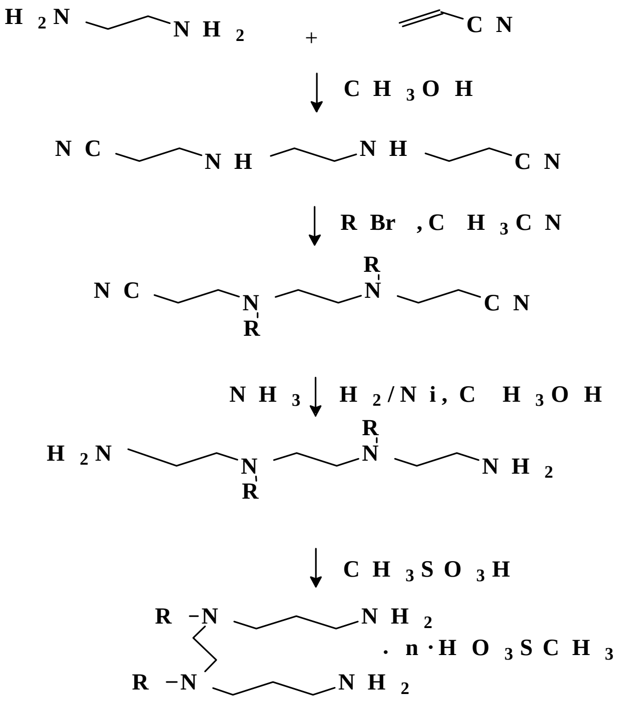	I II III IVa-c
a: R = C_8H_{17} **b: R = $C_{12}H_{25}$** **c: R = $C_{16}H_{33}$**	

Table 2. Physicochemical properties of the studied cationic gemini surfactants IV a-c

Surfact	R	Formula	m.p. °C	Elemental Analysis, found (calc.) C(%)	H(%)	N(%)	ESI-M [a)] m/z (E+)
IVa	C_8H_{17}	$C_{26}H_{62}O_6S_2$	167.6-8.9	52.93 (52.84)	11.05 (10.58)	9.40 (9.48)	590.9
IVb	$C_{12}H_{25}$	$C_{34}H_{78}O_6S_2$	167.8-9.5	58.15 (58.08)	11.22 (11.18)	7.90 (7.97)	703.2
IVc	$C_{16}H_{33}$	$C_{42}H_{94}O_6S_2$	162.0-4.0	61.96 (61.87)	11.69 (11.62)	6.80 (6.87)	815.4

[a)] Electrospray ionization (ESI) mass spectrometry (Finningan TSQ-700 mass spectrometer)

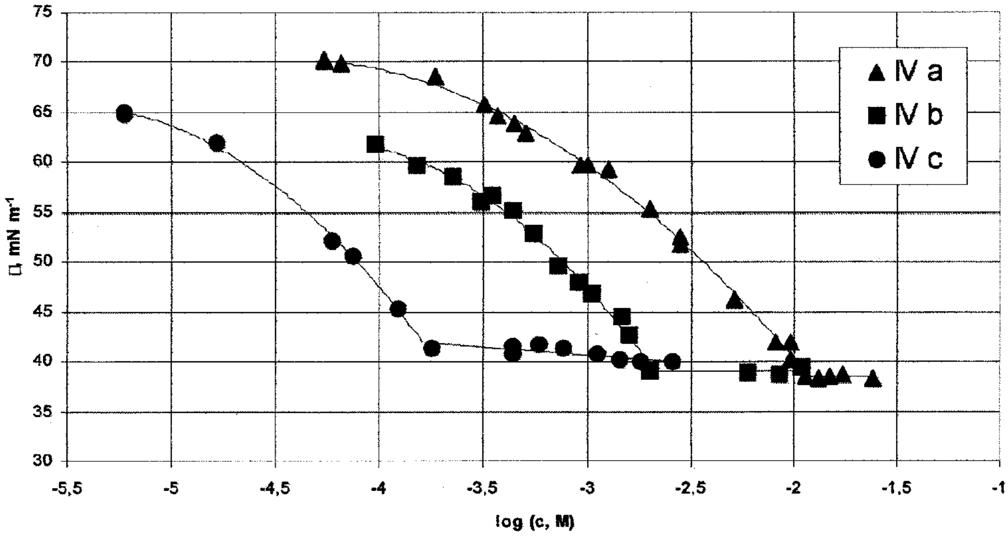

Fig. 1. The surface tension (γ) vs. logarithm of molar concentration (log c) of gemini surfactants IVa-c at 25°C

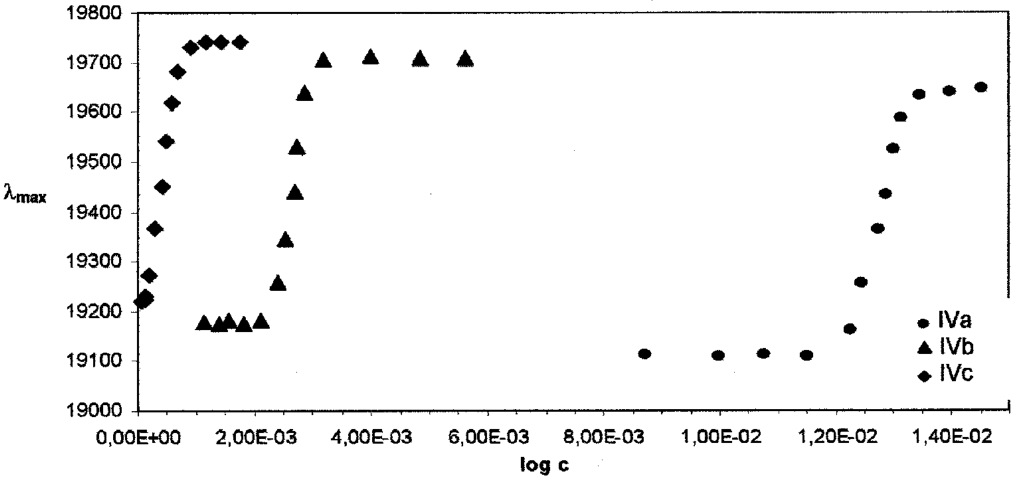

Fig. 2. The wavelength for maximum PRODAN fluorescence intensity as a function of the concentration of IVa-c at 25°C

Accordingly, the fluorescence peak shift in the emission spectra of 6-propionyl-2-(dimethylamino)naphthalene (PRODAN) (λ_{ex} = 360nm) was measured with variation of the given surfactant concentration. The content of the probe was 1.6×10^{-6}M in all cases. The maximum were calculated from the fit of a Gaussian function to the fluorescence spectrum as in (Wong et al. 1999). The plots of the wavelength for maximum PRODAN fluorescence intensity as a function of the concentration of IVa-c at 25°C are shown in the Figure 2. The micelle aggregation numbers, N_{agg}, were obtained by means of the steady-state fluorescence quenching (SSFQ) technique according to (Zana at. al 1997), using Ru(bpy)$_3^{2+}$ as the fluorescence probe and 9,10-diMeA as the fluorescence quencher. Excitation of the probe of a constant concentration (1.0×10^{-6}M) was performed at 415.5nm and the emission was monitored at 638nm (Almgren et. al 1981). Changing the quencher concentration ([Q]) from 0.00 to 5×10^{-4}M a straight line was obtained with a linear relationship between ln[I_0/I_q] and [Q] (Figure 3).

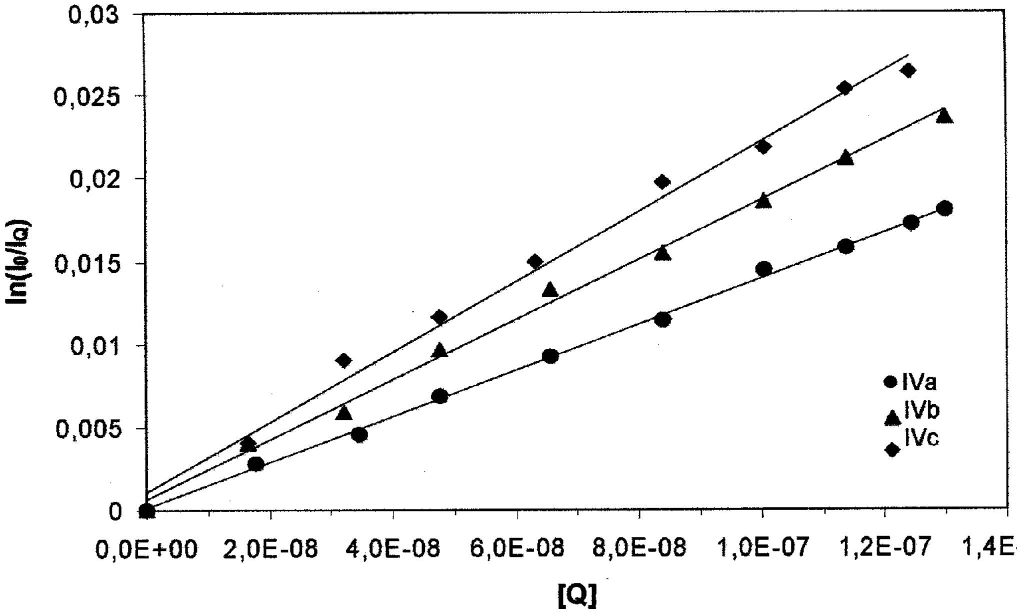

Fig. 3. The luminescence quenching of Ru(bpy)$_3^{2+}$ vs. quencher concentration for aqueous solution of IVa-c at the concentration of surfactants equal to 2.5×cmc$_i$ (i – given compoud) at 25°C.he peak current (diffusion and capacity current), Δi$_p$, vs. surfactant concentration. at 25^{o}C

PCS measurements of micellar properties of IVb-IVc were made on a Zetasizer 3000HS at a temperature of 25°C. The micelle samples were prepared using Fasenius water (this is a pharmaceutical grade water used for irrigation and is extremelly clean and ideal for PCS use). The 0,5% w/v samples were sonicated in a bath sonicater for 5 minutes to aid dispersion of the powder to form micelles. Then, the samples were filtered through an Anotop® 100 nm pore size filter remove unwanted larger particles so that measurement of the micelles was possible. Count rates of approximately 87kcps (kilo counts per second) were obtained with a pinhole of 400 μm, for IVc surfactant and 30kcps for IVb. The emulsion parameters, i.e., the multimodal size distribution and effective diameter of the microdroplets in the system: n-tetradecane/water/surfactant IVa-c (0.005 wt.-%) as a function of oil concentration and time were studied by means of the ZetaPlus (Brookhaven Instrument Co., NY, USA) apparatus, which operates in dynamic scattering mode. The emulsions were prepared in an ultrasonic bath and their effective diameter was measured after 5, 15, 30, 60 120 min, and 1 day of preparation. Following the size distribution, the zeta potential was also calculated. The experiments were all carried out at 25 ^{o}C.

RESULTS AND DISCUSSION

ADSORPTION AT THE SOLUTION-AIR INTERFACE

The plots of surface tension (γ) vs. log c (bulk phase concentration) of aqueous solutions of the studied surfactants IV a-c at 25^{o}C are shown in Figure 1. The surface activity of the dimeric compounds increases with the increase of the alkyl chain length R. The surface tension data provided possibilities to calculate the maximum surface excess concentration Γ_{max} of surfactants at the aqueous solution-air interface from the maximum slope in each case by the use of the relationship (Chattoraj 1966):

$$\Gamma_{max} = [d\Pi \,/\, d(\ln c + \ln y_{\pm})] \,/\, f\,RT \qquad (1)$$

where R is the gas constant at the absolute temperature T, π is the surface pressure in N m^{-1} (π=γ_o -γ, where γ_o is the surface tension of water at 25 ^{o}C), f=1+1/(1+r), r is the ratio between the molar concentration of added salt and the molar concentration of surfactant in the solution, and y± is the mean activity coefficient evaluated from the Debye-Huckel limiting law equation valid for 1:1 electrolytes (Eq.2) (Horvath 1985):

$$\log y_{\pm} = (\log y_{+} + \log y_{-}) / 2 = -\,0.509\,(I)^{1/2} \qquad (2)$$

where I is the ionic strength.

The Π minimum surface area per molecule at the aqueous solution-air interface, A (m^2/molecule), is then calculated from

$$A_{min}=1/(N_A\Gamma_{max}) \qquad (3)$$

where N_A is Avogadro’s number.

The values of effectiveness in surface tension reduction π_{cmc}, surface excess concentration, Γ_{cmc}, surface area demand per molecule A_{min} for the studied surfactants IV a-c are listed in Table 3. The effectiveness of surface tension reduction for IV increases with increasing hydrophobic alkyl chain length R. The cross-sectional area (A_{min}) of IV are not constant across the homologous series but decrease with increasing chain length due to an increasing van der Waals interaction.

MICELLAR AGGREGATION

The studied gemini surfactants IV aggregate in water. Their solutions are clear and nonviscoelastic under the studied conditions. In Table 3 we summarize the cmc values determined for IV by means of the surface tension (Figure 1) and the steady-state fluorescence technique. In case of the latter the cmc values were determined from plots of the wavelength for maximum PRODAN fluorescence intensity vs. IVa-c concentration (Figure 2). Each of the studied surfactants, according to present isotherms in Figure 3, has a well-defined cmc_0 marking the onset of the formation of premicellar aggregates.

Table 3. Parameters of adsorption and micelle formation of the cationic gemini surfactants Iva-c

Surfactant	R	cmc mM	$-\Delta G^o_{cmc}$ kJ mol^{-1}	γ_{cmc} mN m^{-1}	$10^{20}A_{min}$ m^2	Fluorescence	
						cmc,mM	N_{agg}
IVa	C_8H_{17}	11.5	52.7[b)]	38.4	80	12.1	24[f)] 42[g)]
IVb	$C_{12}H_{25}$	2.0	65.7[b)]	39.1	82	2.1	30[f)] 48[g)]
IVc	$C_{16}H_{33}$	0.11	87.1[b)]	40.8	86	0.12	36[f)] 54[g)]
$RN^+(CH_3)_3Br^-$	$C_{10}H_{21}$	67[a)]	13[c)]	40[d)]	-		
$RN^+(CH_3)_3Br^-$	$C_{12}H_{25}$	15[a)]	21[c)]	39[d)]	52[e)]		
$RN^+(CH_3)_3Br^-$	$C_{14}H_{29}$	4[a)]	27[c)]	38[d)]	52[e)]		
$RN^+(CH_3)_3Br^-$	$C_{16}H_{33}$	1[a)]	34[c)]	40[d)]	49[e)]		

a) From Ref. (van Os et. al 1993).
b) From Eq. (4) for $Q = 4$, $\nu = 3$.
c) From Eq. (4) for $Q = 1$, $\nu = 2$.
d) From Ref. (Dam et. al 1996).
e) Surface tension (plate) method, from Ref. (Sokołowski 1995)
f) Determined for [surfactant] = 25 x cmc.
g) Determined for [surfactant] = 25 x cmc.

The cmc value provides a measure for the Gibbs energy of transfer (ΔG^o) of a surfactant from aqueous phase to the micellized state. Dam et al. (1996) have shown that if we assume ideal solution bahavior, aggregation number N is larger then 30, and that the micelles have zero electric charge (α=1), ΔG^o for micelle formation of surface active ionic salt $\nu_+ AM^{z+} \nu_- X^{z-}$ is equal to:

$$\Delta G^o_{cmc} = \nu RT \ln(Q\, x_{cmc}) \tag{4}$$

$$\nu = \nu_+ + \nu_- \tag{5}$$

$$Q = (\nu_+)^{\nu+} (\nu_-)^{\nu-} \tag{6}$$

where ν_+ is the number of moles of cation produced upon complete dissociation of one mole of surfactant, ν_- is the number of moles of anions produced upon complete dissociation of one mole of surfactant, z^+ is the charge number for the cation, z^- is the charge number for the anion, and α is the ionization degree. For the studied gemini surfactants $\nu = 3$, $\nu_+ = 1$ and $\nu_- = 2$ and hence $Q = 4$. Values of ΔG^o for the studied surfactants IV a-c and the conventional cationic surfactants are listed in Table 3.

The aggregation numbers, N_{agg}, of studied IVa-c micelles have been obtained from steady-state fluorescence quenching measurements. As can be seen in Table 3, the N_{agg} values for the micellar solutions of the tested cationic gemini compounds are found to be slightly depending upon the alkyl chain length. It is generally known that the micelle aggregation numbers for dimeric surfactants are larger than for the corresponding monomers, reflecting a much stronger tendency to micelle growth to elongeted and threadlike aggregates (Zana 1995, Danino 1995). However, under the experimental conditions the obtained N_{agg} for studied gemini surfactants correspond to the values expected for the spherical micelle (Alami 1993). For example, at low surfactant concentration (c=2.5×cmc) used in present study, the N_{agg} achieve the values in the range of 24-36 and increase to 42-54 for the ten fold higher concentration. Such a concentration-dependent change in IVa-c micelle size requires further investigations using other techniques, i.e., time-resolved fluorescence quenching and small-angle neutron scattering.

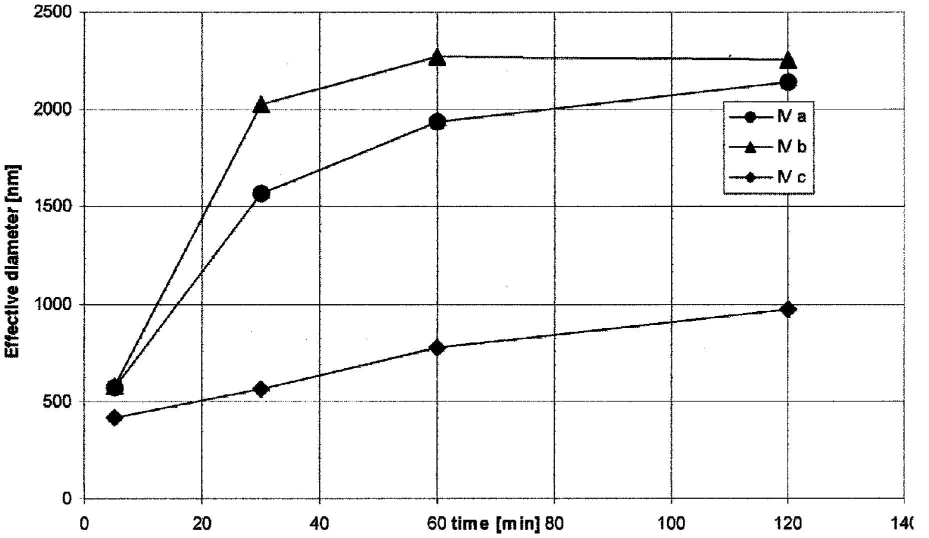

Fig. 4. The effective diameter of n-tetradecane/water/surfactant IVa-c emulsion vs. time

EMULSION SYSTEMS

In this part of studies we have performed experiments describing stability of o/w emulsions: n-tetradecane/water/surfactants IV a-c, as the function of oil concentration and time. The effective diameter (Figure 4) and zeta potential (Figure 5) of n-tetradecane droplets in the studied systems containing 0.005 wt-% of gemini surfactants oscillate from 22 to 2300 nm and from –6 to +15 mV, respectively.

The changes of zeta potentials in all studied emulsions are not monotonic and does not influence the effective diameter of the oil droplets. Generally, zeta potential increases from negative (ca.-5mV) to positive (+14 mV) values vs. time. The effective diameter as a function of oil concentration is presented in Figure 6. The most stable n-tetradecane/water/IVa emulsions were obtained for system containing 10 wt-% of oil. After 30 min, a bimodal distributions is evident due to the coalescence. Bigger droplets than 3000nm move up to the surface where they are not visible for laser beam of instrument.

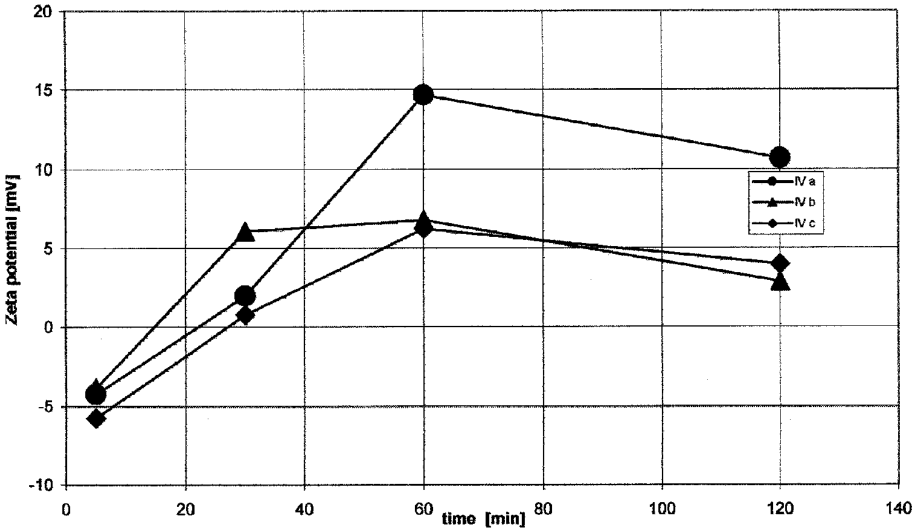

Fig. 5. The zeta potential of n-tetradecane/water/surfactant IVa-c emulsion vs. time

PCS MEASUREMENTS

Table 4 shows the results obtained from 4 repeated measurements at 25°C. The count rates, z-average diameters and polydispersities are all very repeatable indicating that the sample is stable between measurements. The z-average diameters and polydispersity values were obtained using the cumulants analysis according to ISO 13321 Part 8 1996 (International Standard on Determination of Particle Size Distributions by PCS). The size distributions displayed are intensity distributions and were obtained from the correlation functions by analysis with the CONTIN algorithm. Passes were obtained with the Result Quality Factor for all four measurements (see later for details about the Result Quality Factor). The intensity distributions are bimodal consisting of a large peak (approximately 98% of the population) with a mean at 2.7nm and a second, much smaller peak (2% of the population) at 102nm. The mode of these two peaks are at approximately 3 and 80nm respectively. The second, smaller peak is probably due to the continued presence of poorly dispersed surfactant. Zetasizer reports for each measurement are provided together with an overplot of the four measurement.

Table 4: IVc 0.5% w/v Zetasizer 3000HS using 400 μm pinhole

Run Number	Count Rate (kcps)	z-average diameter (nm)	Poly-dispersity	Intensity Mean Peak l(nm)	%of distr.	Intensity Mean Peak 2 (ran)	%of distr.
1	87.2	4.5	0.582	2.7	98.5	102.4	1.5
2	87.0	4.5	0.587	2.7	98.1	82.5	1.9
3	86.7	4.4	0.588	2.6	98.2	91.1	1.8
4	86.9	4.5	0.593	2.7	98.5	102.7	1.5
Mean	86.9	4.5	0.587	2.7	98.3	94.7	1.7
	0.2	0.1	0.005	0.05	0.21	9.7	0.21

Table 5: IVb 0.5% w/v Zetasizer 3000HS using 400 μm pinhole

Run Number	Count Rate (kcps)	z-average diameter (nm)	Poly-dispersity	Intensity Mean Peak l(nm)	%of distr.	Intensity Mean Peak 2 (ran)	%of distr.
1	30.5	4.5	0.541	4.9	100	-	-
2	30.4	4.6	0.522	4.4	100	-	-
3	30.4	4.6	0.515	4.1	100	-	-
4	30.4	4.6	0.526	3.9	99.6	199.7	0.4
Mean	30.4	4.6	0.526	4.3	99.9	-	-
	0.1	0.1	0.011	0.4	0.2	-	-

PCS measurements for IVc

Run	Angle	KCps.	Zave	Poly	Fit	Time
1	90	87.2	4.5	0.582	0.001622	11:39:47
2	90	87	4.5	0.587	0.000977	11:48:12
3	90	86.7	4.4	0.598	0.001411	12:05:03
4	90	86.9	4.5	0.593	0.001979	12:22:03
Avarage		86.9	4.5	0.587		
+/-		0.2	0.1	0.005		

PCS measurements for Ivb

Run	Angle	KCps.	Zave	Poly	Fit	Time
1	90	30.5	4.5	0.541	0.00283	13:29:33
2	90	30.4	4.6	0.522	0.001775	14:00:23
3	90	30.4	4.6	0.515	0.002234	14:15:56
4	90	30.4	4.7	0.526	0.001678	15:02:38
Avarage		30.4	4.6	0.526		
+/-		0.1	0.1	0.011		

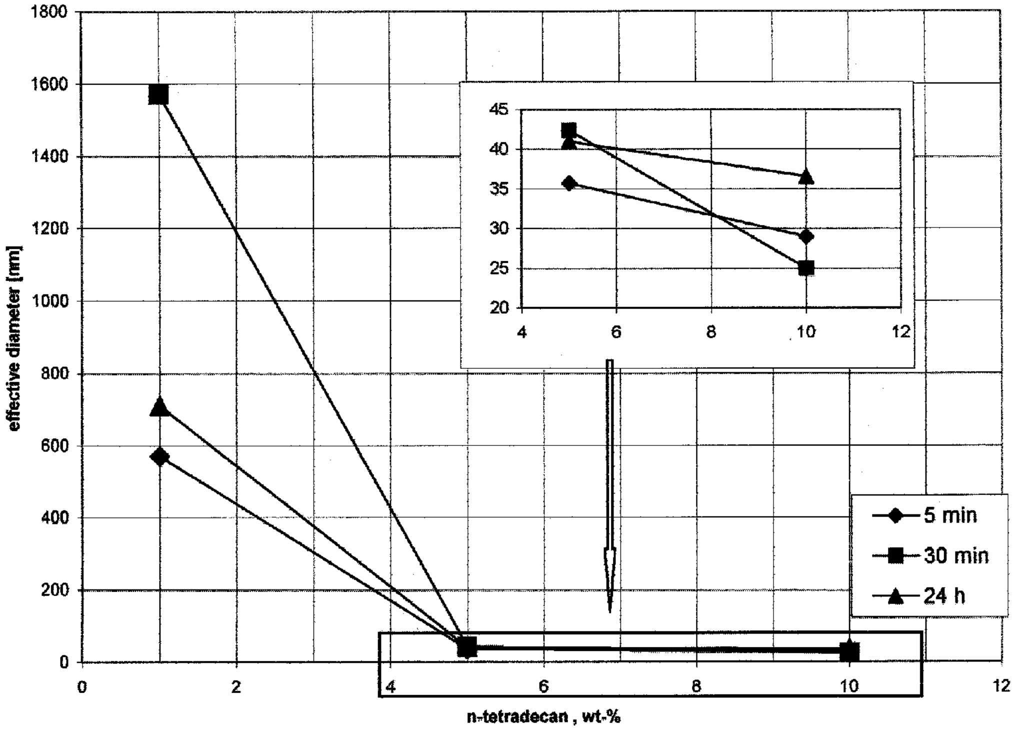

Fig. 6. The effective diameter of tetradecane/water/surfactant IVa emulsion vs. oil concentration

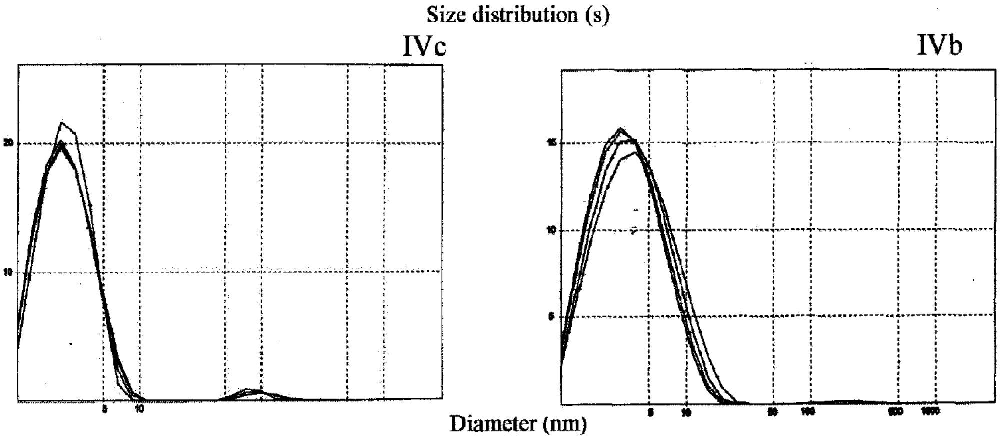

Fig. 7. PCS measurements

Table 5 shows the results obtained from four repeat measurements at 25°C. The count rates, z-average diameters and polydispersities are all very repeatable indicating that the sample is stable between measurements. The size distributions (Figure 7) displayed are intensity distributions and have been obtained from the correlation functions by analysis again with the CONTIN algorithm. Passes were obtained with the Result Quality Factor for all four measurements (see later for details about the Result Quality Factor).The intensity distributions are monomodal apart from the 4th measurement which has a very small peak at around 200nm (however this consists of less than 1% of the distribution). Zetasizer reports for each measurement are provided together with an overplot of the four measurements. Information about the numbers quoted on the reports is provided later in this document.

CONCLUSION

The studied cationic surfactants show moderate tendency to form micelles. Influence of the hydrophobic alkyl chain length upon the cmc and emulsification ability is not as effective as in the case of conventional cationics.

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Nowe kationowe surfaktanty gemini zbudowane z dwóch grup metylosulfonowych oraz z dwóch długich łańcuchów alkilowych (oktylowy, dodecylowy, lub hexadecylowy) zostały zsyntetyzowane z dobrą wydajnością w reakcji N,N'-bis-alkilo-N,N'-bis(3-aminopropylo)etylenodiaminy z kwasem metylosulfonowym. Wszystkie sole "gemini" wykazały dobrą rozpuszczalność w wodzie. Ich zdolność agregacyjną w wodzie oznaczono metodą SSFS. Ich micelarne właściwości powyżej cmc scharakteryzowano przez oznaczenie liczby agregacji $N_{agg.}$ Obecność podwójnych segmentów w cząsteczce surfaktantów odpowiada za ich niezwykłe właściwości fizykochemiczne. Surfaktanty są bardzo efektywne w procesie adsorpcji powierzchniowej jak również przy tworzeniu miceli w wodzie.

Zarówno zdolność do tworzenia miceli jak również do obniżania napięcia powierzchniowego wzrasta wraz ze wzrostem długości łańcucha hydrofobowego. Badane surfaktanty stanowią wielki krok do otrzymywania stabilnych oraz powtarzalnych form emulsji n-tetradekanu. Do określenia najbardziej stabilnych form tychże surfaktantów posłużono się pomiarami potencjału zeta, średnicy efektywnej oraz dimodalnej metody rozrzutu w układzie n-tetradekan/woda/surfaktant.