Supramolecular systems of amphiphilic derivatives of calix[4]resorcinarenes and surfactants in chloroform

I. S. Ryzhkina,[a]★ A. P. Timosheva,[a] A. V. Chernova,[a] R. R. Shagidullin,[a] A. A. Gazizova,[a] W. D. Habicher,[b] T. Krause,[b] L. I. Vagapova,[a] and A. I. Konovalov[a]

[a]A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center of the Russian Academy of Sciences, 8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation. Fax: +7 (843) 273 2253. E-mail: ryzhkina@iopc.kcn.ru
[b]Institut für Organische Chemie, Technische Universität Dresden, 13 Mommsenstraβe, D-01062 Dresden, Germany. Fax: +49 (351) 463 4093

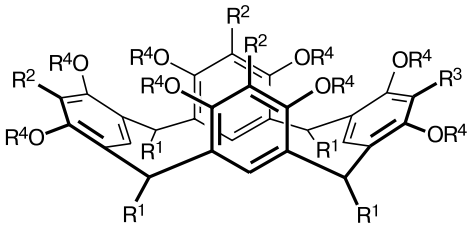
Aggregation of amphiphilic calix[4]resorcinarenes (CRA) modified by carboxymethyl (**1**), 2-hydroxyethyl (**2**), methylamino acetal (**3**), and aminomethyl (**4**) fragments and their interaction with some synthetic (**5**, **6**) and natural (**7**, **8**) surfactants in the low-polarity solvent (chloroform) were studied by permittivity measurements and FT-IR spectroscopy. Compounds **1—4** and surfactants form aggregates at critical micelle concentrations (CMC) of $2.0 \cdot 10^{-5}$—$7.5 \cdot 10^{-5}$ and $1.7 \cdot 10^{-5}$—$2.0 \cdot 10^{-3}$ mol L^{-1}, respectively. The CMC values of CRA—surfactant mixed aggregates depend on the surfactant structure and the structure and concentration of CRA. Analysis of the IR spectra of solutions of a series of amphiphilic CRA (**2—4**, **9**, **10**) and their mixtures with the cationic surfactant *N*-cetyl-*N*,*N*-dimethyl-*N*-(2-hydroxyethyl)ammonium bromide (**5**) showed that an increase in the concentration of the solutions in individual and mixed systems is accompanied by a decrease in the molar integral intensities and intensities in the maxima of the absorption bands of the O—H and C—H bonds down to the CMC point, after which these values change slightly. The discovered effect, which is differently pronounced for all systems studied, indicates that both the polar "head" groups and nonpolar fragments of CRA and surfactant are involved in the formation of supramolecules of the reverse micelle type in all cases.

Key words: supramolecular systems, reverse micelles, micelle formation, amphiphilic calix[4]resorcinarenes, surfactants, chlroform, permittivity measurements, FT-IR spectroscopy.

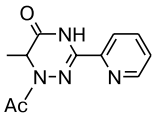
Synthetically available calixarenes are the organized in a complicated manner three-dimensional macrocyclic phenols that are able to form with ions and neutral molecules supramolecular aggregates modeling functions of complex biomolecules, for instance, transport[1] or catalytic[2] functions. We have earlier[3,4] shown that amphiphilic aminomethylated calix[4]resorcinarenes (CRA) in aqueous and organic media are micelle forming surfactants. These compounds can react with synthetic surfactants, such as cetyltrimethylammonium bromide and Triton-X-100, to form mixed supramolecular aggregates with high catalytic activity in hydrolysis of *p*-nitrophenyl esters of phosphorus acids.[5—7] Interest in processes of self-organization in solutions of surfactant mixtures[8] and compounds of complicated molecular architecture has recently increased considerably[1,9,10] primarily due to steady demands of modern nano- and biotechnologies for new polyfunctional reagents. Therefore, studies of aggregation of new amphiphilic derivatives of calix[4]resorcinarene and their interaction with synthetic and natural surfactants seems very urgent.

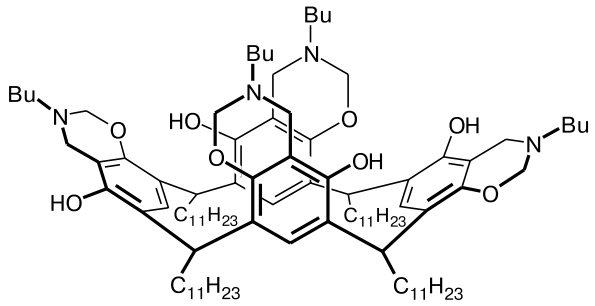
The purpose of the present work is to study the aggregation of a series of amphiphilic CRA modified by carboxymethyl (**1**), 2-hydroxyethyl (**2**), methylamino acetal (**3**), and aminomethyl (**4**) fragments in the absence and presence of synthetic surfactants (*N*-cetyl-*N*,*N*-dimethyl-*N*-(2-hydroxyethyl)ammonium bromide (**5**), Triton-X-100 (**6**)) and natural membrane lipids (phosphatidylcholine (**7**), sodium deoxycholate (**8**)) in a medium of the low-polarity solvent (chloroform). Permittivity measurements and FT-IR spectroscopy served as methods of investigation. The influence of the structure and concentration of CRA and the surfactant structure on the aggregation in individual and mixed systems was estimated.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 459—466, March, 2007.
1066-5285/07/5603-0475

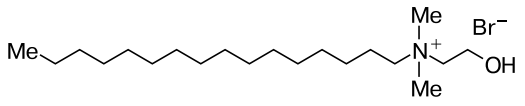


1—4, **9**

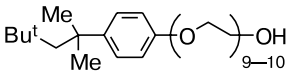
1: $R^1 = C_8H_{17}$, $R^2 = R^3 = H$, $R^4 = CH_2C(O)OH$
2: $R^1 = C_{11}H_{23}$, $R^2 = R^3 = H$, $R^4 = CH_2CH_2OH$
3: $R^1 = C_{11}H_{23}$, $R^2 = R^3 = CH_2N(Me)CH_2CH(OMe)_2$, $R^4 = H$
4: $R^1 = C_{11}H_{23}$, $R^2 = R^3 = CH_2NMe_2$, $R^4 = H$
9: $R^1 = C_9H_{19}$, $R^2 = H$, R^3 =  , $R^4 = H$



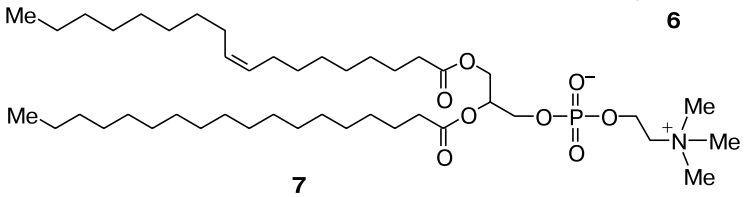
10



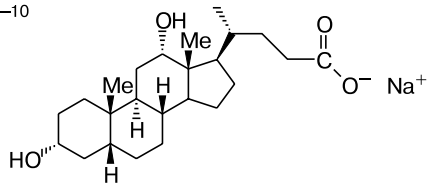
5



6



7



8

Experimental

Calix[4]resorcinarenes **1—4**, **9**, and **10** [11—14] and surfactant **5** [15] were synthesized according to earlier described procedures. Chemically pure samples of Triton-X-100 (**6**) (Sigma), egg (vitellus) phosphatidylcholine (**7**) (>98%, Sigma), and sodium deoxycholate (**8**) (98%, Lancaster) were used. Chloroform was purified by a standard method.[16] Association of compounds **1—4** in the absence and presence of surfactants **5—8** in chloroform was studied by permittivity measurements, *i.e.*, obtaining and subsequent analysis of concentration dependences of the dielectric constant (ε) of compounds **1—8** and their mixtures.[17] Dielectric constants of a series of solutions were determined on a setup consisting of an E12-I instrument operating according to the beat method and a measuring cell, being a temperature-controlled capacitor. The error of the CMC values determined by the accuracy of preparation of concentrations of solutions using a method of series dilution and the accuracy of determination of the dielectric constant of the solutions did not exceed 2%. The IR spectra of compounds **2—4**, **9**, and **10** and their mixtures with compound **5** (in KBr and in $CHCl_3$) were recorded on a Vector-22 FT-IR spectrometer (Bruker); resolution 1 cm^{-1}, accumulation 64 scans; detection time 16 s. The molar integral absorption intensity a was obtained from the surface area of the band $S = \int \log(I_0/I)\nu d\nu$ using the Bouger—Lambert—Beer law ($S = adC$, where d is the layer thickness (cm), and C is the concentration in the solution (mol L^{-1})).[18] The molar absorption coefficient k in the maximum of the band was calculated from the equation $\log(I_0/I) = kcd$, where $\log(I_0/I)$ is the absorbance in the maximum of the band.[18] The statistically estimated[19] relative error for k measurement was 2%, and the error of measurement of the integral intensity was 5—10% depending on the a value.

Results and Discussion

The method of permittivity measurements detecting changes in the dielectric constant of the medium[17] was used to study the aggregation of amphiphilic CRA **1—4** and their mixtures with surfactants **5—8** in chloroform as in the previous works,[4,7] where the aggregation of CRA **9** and **10** was studied. The critical micelle concentration (CMC) was determined from the characteristic breaks in the CMC points in the plots of ε *vs.* concentration of the studied substance $\varepsilon = f(C)$.[4,7,20,21] This type of plots with the pronounced CMC point is observed for compounds **1—8** in chloroform. This indicates that in this solvent all of them behave as micelle forming surfactants that form reverse micelles in low-polarity solvents.[20,21] The plots of ε *vs.* concentration of compound **7** in the absence and presence of CRA **4** are presented in Fig. 1 as an example. The CMC values for compounds **1—8** and mixed systems based on these compounds are summarized in Table 1.

The CMC values and $\varepsilon = f(C)$ curves of CRA derivatives **1—4** ($2.0 \cdot 10^{-5}$—$7.5 \cdot 10^{-5}$ mol L^{-1}) are comparable with the data for the nonionogenic surfactant Triton-X-100 **6** ($6 \cdot 10^{-5}$ mol L^{-1}).[4] The CMC values of CRA depend on the structure and number of introduced polar functional groups and are substantially lower than

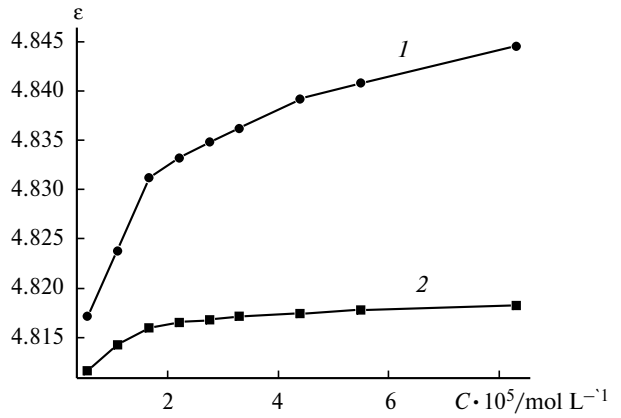


Fig. 1. Change in the dielectric constant of solutions of phosphatidylcholine **7** in chloroform in the absence (*1*) and presence of calix[4]resorcinarene **4** (*2*); $C_4 = 1 \cdot 10^{-4}$ mol L^{-1}.

the CMC ($5 \cdot 10^{-4}$ mol L^{-1}) of the initial unsubstituted calix[4]resorcinarene.[4] Compounds **1** and **2** form aggregates in the region of the CMC point, which lies approximately threefold lower than those of aminomethylated calixarenes **3** and **4**. Probably, CRA **1** and **2**, each having eight terminal carboxyl and hydroxyl groups, are more capable of forming intermolecular hydrogen bonds than compounds **3** and **4** each containing four aminomethyl fragment and forming, hence, as known,[22] strong intramolecular hydrogen bonds (IMHB) OH...N.

The study of micelle formation by surfactants **5—8** with different structures of polar and nonpolar groups showed that the $\varepsilon = f(C)$ plot for zwitterionic phospholipid **7** (unlike CRA **1—4** and surfactants **5**, **6**, and **8**) is stepped and characterized by two CMC values: $1.7 \cdot 10^{-5}$ and $4.5 \cdot 10^{-5}$ mol L^{-1}. The CMC values of synthetic nonionogenic surfactant **6** and zwitterionic phospholipid **7** are close and almost two orders of magnitude lower than the CMC of the ionic surfactants, namely, cationic **5** and anionic **8** ($3 \cdot 10^{-3}$ and $2 \cdot 10^{-3}$ mol L^{-1}, respectively). This confirms an important role of electrostatic interactions for micelle formation in chloroform.[20,21] Substantial differences in the micelle formation ability of the nonionogenic and ionic surfactants are also observed in aqueous and water-organic solvents,[3] although the role of electrostatic interactions during micelle formation of the amphiphilic compounds differs in water and low-polarity solvents of the chloroform type.[21]

Table 1. Critical micelle concentrations for calix[4]resorcinarenes **1—4**, surfactants **5—8**, and related mixed systems in chloroform*

Compounds	CMC /mol L^{-1}	Compounds	CMC /mol L^{-1}
1	$2.0 \cdot 10^{-5}$	**6—3**	$3.5 \cdot 10^{-5}$
2	$2.5 \cdot 10^{-5}$	**6—4**	$2.0 \cdot 10^{-5}$
3	$7.5 \cdot 10^{-5}$	**7**	$1.7 \cdot 10^{-5}$; $4.5 \cdot 10^{-5}$
4	$7.0 \cdot 10^{-5}$	**7—1**	$2.0 \cdot 10^{-5}$; $4.0 \cdot 10^{-5}$
5	$3.0 \cdot 10^{-3}$	**7—2**	$2.5 \cdot 10^{-5}$
5—1	$2.0 \cdot 10^{-3}$	**7—3**	$2.5 \cdot 10^{-5}$
5—2	$8.0 \cdot 10^{-4}$	**7—4**	$1.6 \cdot 10^{-5}$
5—3	$8.0 \cdot 10^{-4}$	**8**	$2.0 \cdot 10^{-3}$
5, **4**	$1.5 \cdot 10^{-3}$	**8—1**	$1.0 \cdot 10^{-3}$
6	$6.0 \cdot 10^{-5}$	**8—2**	$1.3 \cdot 10^{-3}$
6—1	$2.5 \cdot 10^{-5}$	**8—3**	$2.0 \cdot 10^{-3}$
6—2	$3.5 \cdot 10^{-5}$	**8—4**	$1.5 \cdot 10^{-3}$

* The concentrations of CRA in the mixed systems are $1 \cdot 10^{-4}$ mol L^{-1}, *i.e.*, higher than the CMC in individual solutions.

The interaction of surfactants **5—8** with calixarenes **1—4** was estimated from a decrease in the CMC value of the surfactant in the presence of calixarenes.[4,7] Stronger changes in the CMC (by 3—4 times) were observed for mixed systems based on a synthetic surfactant (cationic **5** and nonionogenic **6**) than for a natural surfactant (anionic **8** and zwitterionic **7**), which are less prone to the formation of mixed micelles with CRA. Probably, the formation of mixed supramolecular aggregates CRA—surfactant is rather strongly affected by steric strain of a surfactant molecule, which is much higher for natural lipids **7** and **8** than that of synthetic detergents **5** and **6**.

As can be seen from the data in Table 1, the CMC value of the mixed CRA—surfactant systems depends to a great extent on the structure of introduced CRA and its aggregation state. For instance, CRA **1** containing carboxymethyl fragments manifests pronounced specificity in the formation of mixed micelles with representatives of membrane lipids (sterols and phospholipids). This compound do not virtually react with phosphatidylcholine **7** but shifts the CMC point of sodium deoxycholate **8** noticeably stronger than other CRA (see Table 1). The absence of interaction of CRA **1** with **7** can be judged from the retained two-step shape of the $\varepsilon = f(C)$ plot for **7** in the presence of CRA **1** and the CMC values of the mixed system, which are virtually the same as the CMC of **7** (see Table 1). All other CRA—**7** systems are characterized by only one CMC value. For the formation of mixed micelles, the selectivity to the type of surfactant charge is manifested by CRA **3** with methylamino acetal groups, which does not interact with anionic sodium deoxycholate but forms aggregates with cationic surfactant **5** at the CMC value by 4 times lower than the CMC of pure **5**. For instance, an additive of CRA **3** (the CMC value of **3** is 7.5 mol L^{-1}, see Table 1) to a solution of **5** with the molecular concentration of CRA ($5 \cdot 10^{-5}$ mol L^{-1}) decreases the CMC value of **5** from $3 \cdot 10^{-3}$ to $1.7 \cdot 10^{-3}$ mol L^{-1}, whereas for the micellar concentration of CRA **3** ($1 \cdot 10^{-4}$ mol L^{-1}) the CMC value of **5** decreases to $8 \cdot 10^{-4}$ mol L^{-1}.

Using the ratio of concentrations of CRA and surfactant in the CMC point of a mixed system as a method for estimation of the composition of mixed micelles,[4] one

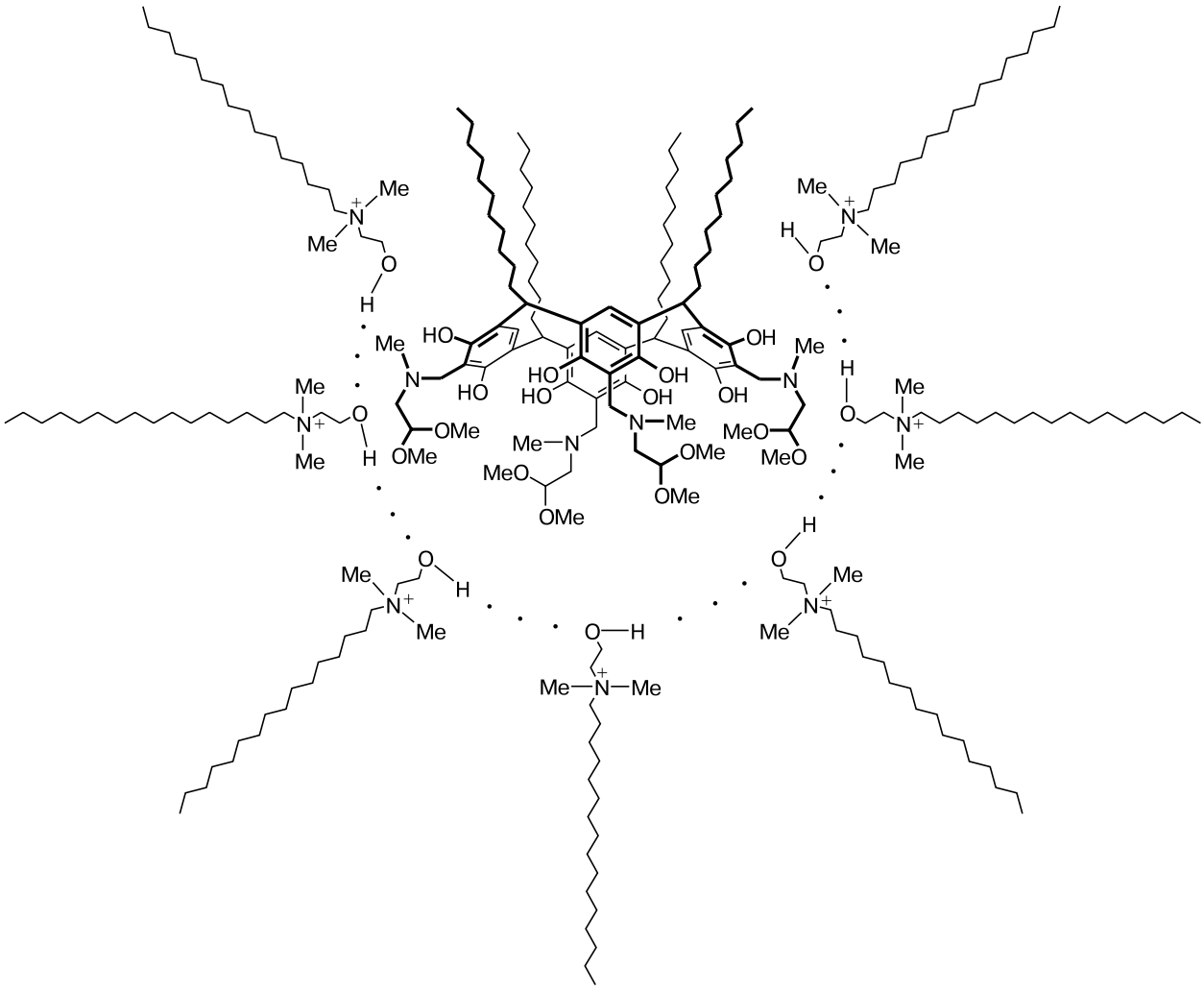


Fig. 2. Scheme of the supramolecular aggregate of the reverse micelle type formed by ionic surfactant *N*-cetyl-*N*,*N*-dimethyl-*N*-(2-hydroxyethyl)ammonium bromide and calix[4]resorcinarene **3** in chloroform.

can suppose that for ionic surfactants **5** and **8** a mixed aggregate is a structure in which one calixarene molecule falls per several surfactant molecules (Fig. 2), whereas for nonionogenic **6** and zwitterionic **7** the situation is opposite (Fig. 3). This presentation of the manner of formation of CRA—surfactant aggregates in chloroform agrees with the "dissociative mechanism" of formation of "capsules" based on unsubstituted CRA and "guest" molecules, namely, alkylammonium or phosphonium salts,[10] and supplements it by a wider range of "guest" and "host" molecules, which can be surfactants and CRA of different structure.

The systems based on several amphiphilic calixarenes including CRA **9** and **10** in addition to CRA **2—4** were studied by FT-IR spectroscopy, as well as mixed systems containing these calixarenes and surfactant **5**. We have earlier[4,7] studied the aggregation in the systems based on CRA **9** and **10** in the absence of **5** and **6** by ^{1}H NMR NOESY and ROESY spectroscopy. For the further analysis of the mechanism of formation of aggregates based on calixarenes and surfactants, the investigation of supramolecular systems was continued using a broader range of calixarenes and one of the most available and informative methods for studying the structure and intermolecular interactions: FT-IR spectroscopy. Surfactant **5** was chosen as a model compound containing the hydroxyl group.

The IR spectra of CRA **2—4**, **9**, and **10** and surfactant **5** correspond to the assumed molecular structure,[23] ν/cm^{-1}: 3400—3200 (OH); 3000—2780, 1470, 720 (CH); 2550 (OH...N); 1610 (Ph); 1360—1230 (C—O, C—C, C—N); 1130—970 (C—N, C—O, C—C), and others. Since the hydroxy groups are active centers of association for all compounds under study in chloroform, in the present work we studied in detail the region of appearance of stretching vibrations ν(OH) for solutions of **2—5**, **9**, and **10** in the range of concentrations close to the

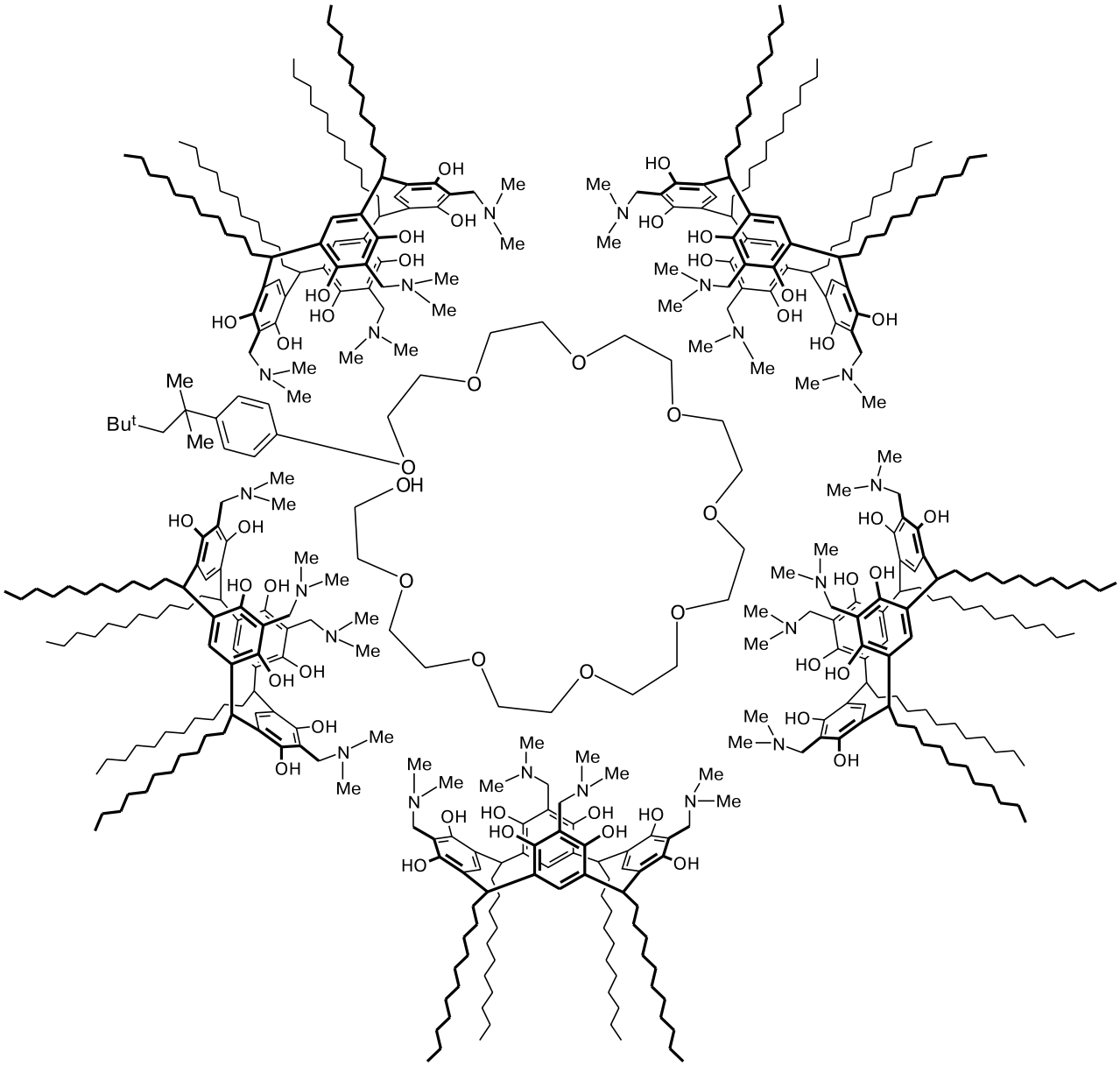


Fig. 3. Scheme of the supramolecular aggregate of the reverse micelle type formed by the nonionogenic surfactant Triton-X-100 and calix[4]resorcinarene **4** in chloroform.

CMC point. In addition to the frequencies, we measured the coefficients of the molar integral (*a*) and peak (*k*) intensities of the ν(OH) bands. For comparison, similar parameters were also obtained for the $\nu(CH_2)$ band at 2855 cm^{-1} corresponding to the hydrocarbon group that is relatively neutral in intermolecular effects (Table 2). As can be seen from the data in Table 2 and Fig. 4, the IR spectra of the studied compounds contain absorption bands at 3400—3200 cm^{-1} typical of the H-bonded OH groups. In addition of the band at 3250 cm^{-1} corresponding to the OH...OH cooperative IMHB, aminomethylated CRA **3** and **4** are characterized by one more very broad low-frequency band with a maximum at ~2600 cm^{-1}, which is the ν(XH) absorption in the O...H...N bridge.[22] This band is observed against the overtones and has a very diffuse contour and, hence, we did not estimate quantitatively its parameters at this stage of investigation. In the spectra of compounds **2—4**, **9**, and **10** in KBr, the ν(OH) frequencies are close to the values observed for the solutions (see Table 2). Analysis of the obtained results shows that no dramatic changes in the spectral pattern in the ν(OH) region were observed on going from the solid phase of compounds **2—4**, **9**, and **10** to their solutions in chloroform. No monomeric forms of

Table 2. Parameters of the bands at 3300 cm^{-1} (ν(OH)) and 2855 cm^{-1} (ν(CH)) in the FT-IR absorption spectra of compounds **2—5**, **9**, and **10**

Compound	ν(OH)/cm^{-1} in KBr	Solutions in $CHCl_3$					
		C /mol L^{-1}	ν(OH) /cm^{-1}	k_{OH}	k_{CH}	k_{OH}/k_{CH}	$a_{OH}\cdot10^{-3}$ /cm $mmol^{-1}$
				cm^2 $mmol^{-1}$			
2	3550 sh,	$2.00\cdot10^{-5}$	3425	429	1739	0.25	115
	3494 sh,	$6.67\cdot10^{-5}$	3429	339	1499	0.23	64
	3347	$3.34\cdot10^{-4}$	3429	294	1485	0.20	62
		$6.67\cdot10^{-4}$	3429	278	1527	0.18	59
3	3271	$4.00\cdot10^{-5}$	3272	483	858	0.56	152
		$1.40\cdot10^{-4}$	3272	388	614	0.58	115
		$4.00\cdot10^{-4}$	3272	359	617	0.58	108
4	3341/3290	$5.00\cdot10^{-5}$	3252	595	2330	0.26	178
		$1.04\cdot10^{-4}$	3252	565	2200	0.26	162
		$5.18\cdot10^{-4}$	3252	532	2090	0.25	126
		$7.85\cdot10^{-4}$	3252	391	1530	0.26	105
5	3336/3243	$2.20\cdot10^{-3}$	3301	247	666	0.37	66
		$8.80\cdot10^{-3}$	3301	192	527	0.36	49
		$2.20\cdot10^{-2}$	3301	179	497	0.36	42
9	3293	$7.00\cdot10^{-5}$	3257	843	804	1.05	284
		$1.40\cdot10^{-4}$	3257	817	817	1.00	288
		$6.80\cdot10^{-4}$	3257	809	809	1.00	245
		$1.00\cdot10^{-3}$	3264	931	942	0.99	285
10	3344	$0.85\cdot10^{-4}$	3345	511	1480	0.35	122
		$1.44\cdot10^{-4}$	3345	504	1430	0.35	107
		$5.13\cdot10^{-4}$	3345	493	1430	0.34	97
		$7.89\cdot10^{-4}$	3345	504	1440	0.35	93

the molecules were observed at 3650—3600 cm^{-1} upon dilution of the solutions.[23] To exclude the disguising effect of distortions upon compensation of H_2O traces in the solution and solvent in this region, we estimated the ratios of intensities of the ν(OH) (~3300 cm^{-1}) and ν(CH) (~2855 cm^{-1}, internal standard) bands. The value of this ratio remains virtually unchanged with dilution of the solutions (see Table 2), although its decrease should be expected for the cleavage of hydrogen bonds. Based on this, one can conclude that ensembles of molecules of CRA **2—4**, **9**, and **10** formed in the solid phase and in solutions involving hydrogen bonding are very strong and do not decompose noticeably with dilution of the solutions. These data agree with the results obtained by the

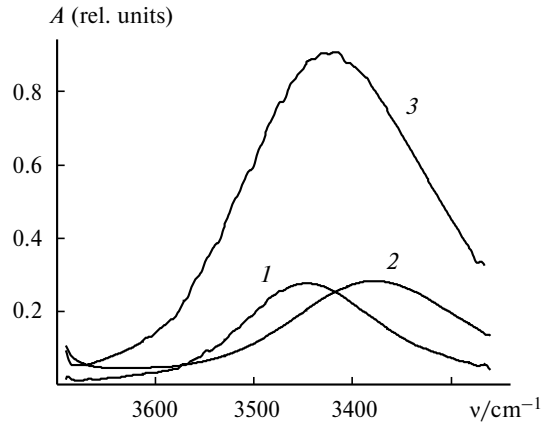


Fig. 4. IR spectra of solutions in chloroform (d = 1 cm) of: *1*, surfactant **5** ($C = 2.1\cdot10^{-3}$ mol L^{-1}); *2*, CRA **10** ($C = 5.0\cdot10^{-4}$ mol L^{-1}); *3*, mixture **5—10** ($C_5 = 3.6\cdot10^{-3}$ mol L^{-1}, $C_{10} = 5.0\cdot10^{-4}$ mol L^{-1}).

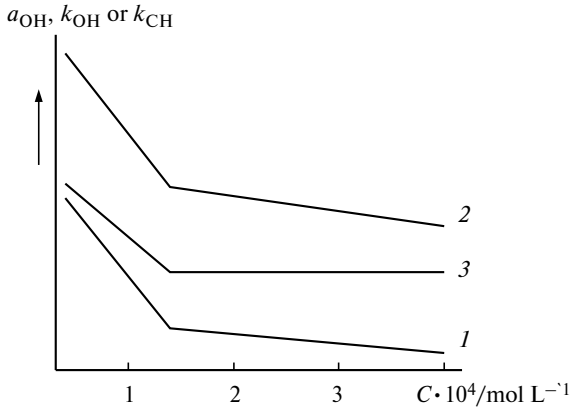


Fig. 5. Dependences of the molar intensities $a_{OH}\cdot10^{-3}$/cm L mol^{-1} (*1*) and k_{OH}/cm^2 $mmol^{-1}$ (*2*) of the band at 3272 cm^{-1} and k_{CH}/cm^2 $mmol^{-1}$ (*3*) of the band at 2863 cm^{-1} in the IR spectra on the concentration of CRA **3** in chloroform solutions.

studies of the concentration dependences in the systems based on CRA **10** in chloroform by ^{1}H NMR 2D NOESY spectroscopy.[7]

A pronounced regularity was found during the study of the dependence of intensities of the discussed bands on the concentration changes and transition through the CMC point. In all series of solutions of **2—5**, **9**, and **10**, the molar coefficients *a* and *k* of the ν(OH) band decrease to this or another extent to the CMC point (see Table 2), after which these values change slightly. The found regularity is clearly illustrated by the plots shown in Fig. 5 for CRA **3**, whose shape is typical of the concentration dependences of the physicochemical properties of surfactant solutions.[24]

The decrease in the intensities (*a* and *k*) of the ν(OH) band is observed for both individual compounds **2—5**, **9**, and **10** and mixtures of CRA **2—4**, **9**, and **10** with surfactant **5** in all cases, except for *k* in the **10—5** mixed system (Table 3). The contribution of the constant component, *i.e.*, CRA, was subtracted when estimating the intensity values for solutions of CRA—surfactant mixtures. This was made to avoid an artificial decrease in the intensity of the discussed band in the mixed system due to a decrease in the fraction of CRA with an increase in the concentration of surfactant **5**.

As mentioned above, the ratio of intensities in the maxima of the bands at 3300 and 2855 cm^{-1} with a change in the concentration of solutions remains constant within an accuracy of measurements (see Table 2). This is illustrated for CRA **3** by parallel changes in k_{OH} and k_{CH} (see Fig. 5). Since in intermolecular interactions the C—H bonds are relatively neutral compared to the very

Table 3. Parameters of the bands at 3300 cm^{-1} (ν(OH)) and 2855 cm^{-1} (ν(CH)) in the FT-IR absorption spectra of mixed CRA—surfactant systems (solutions in $CHCl_3$)

System CRA—surfactant	C_{CRA}	C_5	ν(OH) /cm^{-1}	k_{OH}	k_{CH}	k_{OH}/k_{CH}	$a_{OH}\cdot10^{-3}$ /cm mmol^{-1}
	mol L^{-1}			cm^2 mmol^{-1}			
2—5	$1.5\cdot10^{-4}$ [a]	$5.10\cdot10^{-4}$	3286	164[b]	627[b]	0.26	59
		$1.37\cdot10^{-3}$	3286	153	556[c]	0.27	41
		$2.99\cdot10^{-3}$	3286	149	507[c]	0.29	35
		$8.00\cdot10^{-3}$	3286	146	493[c]	0.29	33
3—5	$1.5\cdot10^{-4}$ [a]	$1.00\cdot10^{-3}$	3284	742[c]	1374[c]	0.54	103[c]
		$4.00\cdot10^{-3}$	3284	297[c]	694[c]	0.43	69[c]
		$8.00\cdot10^{-3}$	3284	245[c]	564[c]	0.43	73[c]
	$3.4\cdot10^{-5}$ [d]	$6.12\cdot10^{-4}$	3275	227[c]	826[c]	0.27	45[c]
		$3.19\cdot10^{-3}$	3284	140[c]	499[c]	0.28	28[c]
		$5.99\cdot10^{-3}$	3285	142[c]	477[c]	0.29	30[c]
4—5	$1.00\cdot10^{-4}$ [a]	$9.20\cdot10^{-4}$	3283	200[c]	590[c]	0.34	58[c]
		$3.60\cdot10^{-3}$	3295	175[c]	450[c]	0.39	45[c]
		$7.50\cdot10^{-3}$	3295	182[c]	535[c]	0.34	44[c]
	$4.8\cdot10^{-5}$ [d]	$9.20\cdot10^{-4}$	3275	156	520[c]	0.30	34[c]
		$3.16\cdot10^{-3}$	3286	153	508[c]	0.30	32[c]
		$6.10\cdot10^{-3}$	3286	150	496[c]	0.30	30[c]
9—5	$1.6\cdot10^{-4}$ [a]	$1.00\cdot10^{-4}$	3322	1162[c]	4394[c]	0.26	77[c]
		$3.60\cdot10^{-3}$	3291	152[c]	490[c]	0.31	40[c]
		$7.20\cdot10^{-3}$	3291	150[c]	465[c]	0.32	37[c]
	$6.0\cdot10^{-5}$ [d]	$1.00\cdot10^{-4}$	3291	1349[c]	4543[c]	0.30	117[c]
		$3.60\cdot10^{-3}$	3291	132[c]	424[c]	0.31	33[c]
		$7.20\cdot10^{-3}$	3291	148[c]	468[c]	0.32	32[c]
10—5	$5.0\cdot10^{-4}$ [a]	$1.00\cdot10^{-3}$	3334	176[c]	575[c]	0.31	83[c]
		$3.60\cdot10^{-3}$	3320	175[c]	489[c]	0.36	58[c]
		$6.96\cdot10^{-3}$	3314	185[c]	516[c]	0.36	50[c]
	$6.0\cdot10^{-5}$ [d]	$1.00\cdot10^{-3}$	3286	112[c]	449[c]	0.25	31[c]
		$2.76\cdot10^{-3}$	3286	140[c]	516[c]	0.27	31[c]
		$6.09\cdot10^{-3}$	3286	143[c]	504[c]	0.28	30[c]

[a] The CRA concentration in the CRA—surfactant system above the CMC.
[b] The contribution of CRA **2** to the intensity of the corresponding band at 3286 cm^{-1} was insignificant and ignored.
[c] The values of the intensity coefficients a_{OH}, k_{OH}, and k_{CH} were obtained for CRA—surfactant solutions with account for the constant component, *i.e.*, CRA.
[d] The CRA concentration in the CRA—surfactant system below the CMC.

active OH groups, the regularity observed is not associated with changes in the structure of the molecules or the mechanism of association due to hydrogen bonding only. The phenomenon is common for all samples and, hence, rough mistakes of sample preparation can be excluded. Thus, the symbate behavior of k_{OH} and k_{CH} indicates the change in the general situation in the system, *i.e.*, micelle formation in which both the polar and nonpolar groups of the molecules are involved. It is known that the Bouger—Lambert—Beer law is strictly fulfilled only for uniform, homogeneous media. In the formed supramolecular aggregates, the surface and internal functional groups interact in different manner with IR radiation: the surface groups interact actively, whereas the internal groups are shielded and interact less actively. As a result, the Bouger—Lambert—Beer law is violated, and the total absorption intensity decreases.[18] This occurs jumpwise in the CMC point, which is illustrated by the plots in Fig. 5. Since no drastic changes in the parameters are observed in the spectra, new ensembles are mainly built, most likely, *via* the available mechanism: formation of hydrogen bonding and universal (van der Waals) interactions.[17] However, there are some specific features. For instance, unlike the peak coefficients, the integral coefficients a_{OH} decrease more sharply with an increase in the concentration of the solutions (see Fig. 5). This fact indicates the narrowing of the ν(OH) absorption bands and, hence, more uniformity of the position of the OH groups in the formed supramolecular ensembles compared to heterogeneities on the surface of the molecules before micelle formation. Evidently, the simultaneously changing situation of dipole-dipole interactions[4] also affects the integral intensity of the ν(OH) band due to the influence of micelle formation on the dipoles of the O—H bonds and, therefore, on the derivative of the dipole moment with respect to the bond determining the absorption intensity.

Although the effect of intensity decrease has a general character, it is differently pronounced for different structures, being from weak to noticeable in the following series: **9**, **10**, **2**, **4**, **3**, **5** (see Table 2). This effect is more pronounced in the CRA—surfactant mixed systems in which it agrees in part with the results obtained by permittivity measurements. For example, according to the data in Tables 1 and 3, the maximum decrease in the intensity coefficients and the maximum shift of the CMC value are observed for the **3—5** system, and the **4—5** system exhibits more moderate effects (see Tables 1 and 3).

In the conclusion, we showed that CRA **1—4** and surfactants form aggregates at CMC values of $2.0 \cdot 10^{-5}$—$7.5 \cdot 10^{-5}$ and $1.7 \cdot 10^{-5}$—$2.0 \cdot 10^{-3}$ mol L^{-1}, respectively; the CMC values of the CRA—surfactant mixed aggregates depend on the surfactant structure and the structure and concentration of CRA. The study of the IR absorption spectra of CRA **2—4**, **9**, and **10** and their mixtures with surfactant **5** in chloroform solutions shows the common phenomenon: with an increase in the concentration of the solutions the molar intensity coefficients of the functionally active O—H bonds and relatively neutral C—H bonds decrease down to the CMC point, which is related to micelle formation with pronounced specific features for different CRA structures. The results obtained indicate that further studies using permittivity measurements and IR spectroscopy are promising for detailed insight in the formation of supramolecular aggregates.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 06-03-32402).

References

1. *Calixarenes 2001*, Eds Z. Asfari, V. Bohmer, and J. Harrowfield, Kluwer Academic Publ., Dordrecht—Boston—London, 2001, 683.
2. I. S. Ryzhkina, T. N. Pashirova, W. D. Habicher, L. A. Kudryavtseva, and A. I. Konovalov, in *Macromolecular Symposia: Reactive Polymers 2003 (Dresden, Germany, 2003)*, Ed. H.-J. P. Adler, Wiley-VCH Verlag GmbH and Co, Weinheim, 2004, 41.
3. I. S. Ryzhkina, Ya. A. Babkina, S. S. Lukashenko, K. M. Enikeev, L. A. Kudryavtseva, and A. I. Konovalov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2002, 2026 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 2183].
4. I. S. Pyzhkina, K. M. Enikeev, A. P. Timosheva, T. N. Pashirova, S. S. Lukashenko, L. A. Kudryavtseva, and A. I. Konovalov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2004, 1470 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 1528].
5. I. S. Ryzhkina, T. N. Pashirova, Ya. A. Filippova, L. A. Kudryavtseva, A. P. Timosheva, V. P. Arkhipov, Z. Sh. Idiyatullin, E. V. Popova, A. R. Burilov, and A. I. Konovalov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2004, 1462 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 1520].
6. I. S. Ryzhkina, L. A. Kudryavtseva, Ya. A. Babkina, K. M. Enikeev, M. A. Pudovik, and A. I. Konovalov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2000, 1361 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 1355].
7. I. S. Pyzhkina, K. M. Enikeev, A. P. Timosheva, T. N. Pashirova, S. S. Lukashenko, L. A. Kudryavtseva, A. I. Konovalov, O. N. Chupakhin, G. L. Rusinov, and N. A. Itsikson, *Zh. Strukt. Khim.*, 2005, **46**, Prilozhenie, 70 [*Russ. J. Struct. Chem.*, 2005, **46**, Supplement (Engl. Transl.)].
8. N. A. Smirnova, *Usp. Khim.*, 2005, **74**, 138 [*Russ. Chem. Rev.*, 2005, **74** (Engl. Transl.)].
9. A. L. Buchachenko, *Usp. Khim.*, 2003, **72**, 419 [*Russ. Chem. Rev.*, 2003, **72** (Engl. Transl.)].
10. L. C. Palmer and J. Rebek, Jr., *Org. Biol. Chem.*, 2004, **2**, 3051.
11. T. Krause, M. Gruner, D. Kukling, and W. D. Habicher, *Tetrahedron Lett.*, 2004, **45**, 9635.
12. A. R. Burilov, L. I. Vagapova, M. A. Pudovik, W. D. Habicher, and A. I. Konovalov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2003, 2155 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 2276].
13. R. Arnecke, V. Bohmer, E. Paulus, and W. Vogt, *J. Am. Chem. Soc.*, 1995, **117**, 3286.

14. O. N. Chupakhin, G. L. Rusinov, and N. A. Itsikson, *Heterocycl. Commun.*, 2004, **10**, 15.
15. H. J. Minch, Sihin-Shin Chen, and R. Peters, *J. Org. Chem.*, 1978, **43**, 31.
16. A. J. Gordon and R. A. Ford, *The Chemist´s Companion. A Handbook of Practical Data, Techniques, and References*, J. Wiley and Sons, New York—London—Sydney—Toronto, 1972.
17. E. N. Gur´yanova, I. P. Gol´dshtein, and I. P. Romm, *Donorno-aktseptornaya svyaz´* [*Donor-Acceptor Bonding*], Khimiya, Moscow, 1973, 156 pp. (in Russian).
18. A. L. Smith, *Fundamentals Techniques and Analytical Problem of Applied Infrared Spectroscopy*, Wiley, New York, 1979.
19. *Pravila YuPAK, Zh. Anal. Khim.*, 1998, **53**, 999 [*IUPAC Rules, J. Anal. Chem.*, 1998, **53** (Engl. Transl.)].
20. A. I. Serdyuk, V. I. Podmarkov, R. V. Kucher, and L. V. Luk´yanenko, *Dokl. Akad. Nauk SSSR*, 1985, **284**, 1430 [*Dokl. Chem.*, 1985, **284** (Engl. Transl.)].
21. *Micellization, Solubilization, Microemulsions*, Ed. K. L. Mittal, Plenum Press, New York, 1977.
22. V. I. Kovalenko, A. V. Chernova, R. R. Shagidullin, G. M. Doroshkina, and E. I. Borisoglebskaya, *Sb. statei 5-i Vseros. konf. "Struktura i dinamika molekulyarnykh sistem"* [*Collection of Articles of the 5th All-Russia Conf. "Structure and Dynamics of Molecular Systems*], Ioshkar-ola, 1998, Part 1, 126 (in Russian).
23. L. J. Bellamy, *The Infra-Red Spectra of Complex Molecules*, 2nd ed., Methuen, London, 1958.
24. *Poverkhnostno-aktivnye veshchestva i kompozitsii, Spravochnik* [*Surfactant Substances and Compositions*], Ed. M. Yu. Pletnev, Klavel´, Moscow, 2002, 768 pp. (in Russian).

Received November 14, 2006;
in revised form February 2, 2007