Aggregation behavior and catalytic activity of systems based on calix[4]resorcinarene derivatives and surfactants.
1. Mixed micellization of aminomethylated calix[4]resorcinarenes with cetyltrimethylammonium bromide in aqueous dimethylformamide

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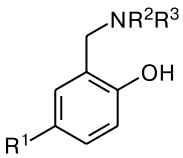
Mixed micellization of amphiphilic aminomethylated calix[4]resorcinarenes and phenols, which are their structural units, with the cationic surfactant cetyltrimethylammonium bromide (CTAB) in aqueous 10—70 vol % DMF decreases the critical micelle concentration; the resulting aggregates are larger than those in the CTAB—DMF—water systems. The micellization of CTAB with aminomethylated calix[4]resorcinarenes proceeds in two steps, while its micellization with phenols is a single-step process. The micellization characteristics depend on the structure and hydrophobicity of the amphiphilic compound and the concentration of DMF.

Key words: micellization, mixed micelles, critical micelle concentrations, amphiphilic compounds, surfactant, aminomethylated calix[4]resorcinarene, *o*-aminomethylphenol, cetyltrimethylammonium bromide.

In recent years, many fundamental and practical problems have been solved by using the so-called membrane mimetic approach[1] involving examination of the properties and behavior of supramolecular systems[2] built from atomic or molecular clusters and model membranes formed by surfactants. Particular attention has been given to systems containing, along with ionic surfactants, water-soluble polymers,[3] cyclodextrins,[4] crown ethers,[5] calix[n]arenes,[6] and porphyrins.[7]

Amphiphilic water-soluble calix[n]arenes form aggregates[8] and are inserted into bilayers of phospholipids.[9] Calix[4]resorcinarenes (resorcarenes) prepared by condensation of resorcinol with an aldehyde are more amphiphilic compounds than "classic" phenol-based calix[4]arenes. In solution, calix[4]resorcinarenes are in the stable cone conformation[10] having a hydrophobic cavity. The presence of four hydrophobic hydrocarbon radicals on the lower rim of the cavity (R^5) and polar or charged functional groups on the upper rim makes them highly amphiphilic and capable of forming ordered mono- and multilayers at interfaces and solid supports with a broad spectrum of practically useful properties.[11] Aggregation of calix[4]resorcinarenes and their derivatives in solutions[12,13] and the effect of micellar media on their aggregation behavior and reactivity remain poorly investigated.[14]

In this work, we studied micellization in the mixed CTAB—AMP and CTAB—AMC systems (CTAB is the cationic surfactant cetyltrimethylammonium bromide,



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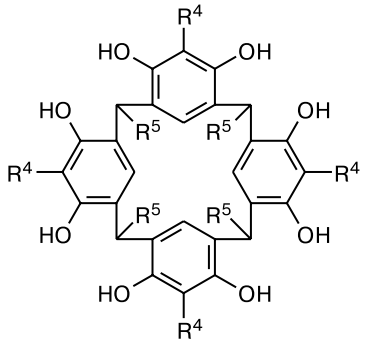

3—6

1: $R^1 = C_9H_{19}$; $R^2 = R^3 = Me$
2: $R^1 = R^2 = H$; $R^3 = C_8H_{17}$

3: $R^4 = CH_2NMe_2$; $R^5 = C_9H_{19}$
4: $R^4 = CH_2NEt_2$; $R^5 = C_{11}H_{23}$
5: $R^4 = CH_2NEt_3$; $R^5 = CH_2P(O)(OPr^i)OH$
6: $R^4 = CH_2NEt_2$; $R^5 = CH_2P(O)(OBu^n)OH$

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AMP are amphiphilic aminomethylated phenols **1** and **2**, and AMC are aminomethylated calix[4]resorcinarenes with hydrophobic (**3**, **4**) and hydrophilic (**5**, **6**) fragments) in aqueous DMF, as well as the effect of the DMF concentration on micellization in these systems.

Experimental

Compounds **1**, **2** [15] and **3**, **4** [16] were prepared according to known procedures. Compounds **5** and **6** were synthesized by aminomethylation[16] of calix[4]resorcinarenes containing phosphorus-bearing alkyl fragments on the lower rim, which were prepared as described earlier.[17] ^{1}H and ^{31}P NMR spectra were recorded on Bruker WM-250 and Bruker CXP-100 instruments (250.13 and 36.45 MHz, respectively) with reference to the signals of residual protons of the deuterated solvent ($CDCl_3$) and with 85% H_3PO_4 as the external standard. The physicochemical properties of compounds **3** and **4** were reported in our previous study.[18]

5,11,17,23-Tetrakis(diethylaminomethyl)-4,6,10,12,16,18,22,24-octahydroxy-2,8,14,20-tetrakis(*O*-propylmethylphosphon-1-yl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (5). The yield of compound **5** was 87%. Found (%): C, 56.47; H, 8.02; N, 4.20. $C_{64}H_{108}N_4O_{20}P_4$. Calculated (%): C, 55.98; H, 7.58; N, 4.08. ^{1}H NMR (250 MHz, $CDCl_3$), δ: 0.84 (m, 8 H, PC$\underline{H}_2$); 1.04 (m, 12 H, $CH_2C\underline{H}_3$); 1.22 (t, 12 H, $NCH_2C\underline{H}_3$, $^3J_{H,H}$ = 7.0 Hz); 1.27 (m, 8 H, C$\underline{H}_2CH_3$); 2.68 (m, 16 H, NC$\underline{H}_2CH_3$); 3.62 (m, 8 H, $C_{arom}C\underline{H}_2N$); 3.92 (m, 8 H, POC$\underline{H}_2$); 4.54 (m, 4 H, CH); 7.15 (br.s, 4 H, *m*-H_{arom}). ^{31}P NMR (36.45 MHz, $CDCl_3$), δ: 32.26.

5,11,17,23-Tetrakis(diethylaminomethyl)-4,6,10,12,16,18,22,24-octahydroxy-2,8,14,20-tetrakis(*O*-butylmethylphosphon-1-yl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene (6). The yield of compound **6** was 72%. Found (%): C, 56.40; H, 8.22; N, 3.94. $C_{68}H_{112}N_4O_{20}P_4$. Calculated (%): C, 57.14; H, 7.84; N, 3.92. ^{1}H NMR (250 MHz, $CDCl_3$), δ: 0.87 (m, 8 H, PC$\underline{H}_2$); 1.09 (m, 12 H, $(CH_2)_2C\underline{H}_3$); 1.20 (t, 12 H, $NCH_2C\underline{H}_3$, $^3J_{H,H}$ = 7.0 Hz); 1.24 (m, 16 H, $(C\underline{H}_2)_2CH_3$); 2.63 (m, 16 H, NC$\underline{H}_2CH_3$); 3.70 (m, 8 H, $C_{arom}C\underline{H}_2N$); 3.82 (m, 8 H, POC$\underline{H}_2$); 4.59 (m, 4 H, CH); 7.18 (br.s, 4 H, *m*-H_{arom}). ^{31}P NMR (36.45 MHz, $CDCl_3$), δ: 32.86.

CTAB was a Fluka chemical (99% purity).

Aminomethylated phenols (AMP) and calix[n]resorcinarenes (AMC) are neither soluble in water nor form micelles in DMF. Hence, their aggregation was investigated in aqueous DMF (10 to 70 vol %). Aggregation in mixed systems consisting of AMP, AMC, phosphorylated AMC (PAMC), and CTAB was studied by conductometry, permittivity measurements, and NMR spectroscopy. The first two methods make it possible to determine characteristic concentrations at which surfactant solutions change from molecular to micellar state, *i.e.*, critical micelle concentrations (CMC);[19] the sizes of the resulting aggregates were estimated by NMR spectroscopy.[20] Critical micele or aggregation concentrations (CMC or CAC) were determined from the characteristic breaks at the CMC (CAC) points in the plots of χ or ε *vs.* the concentration of a compound under study (Figs. 1—3) as described earlier.[21,22] The conductivities χ of solutions were measured on a CDM-2d conductometer at 30±0.1 °C; the temperature was maintained with the use of a U1 thermostat. Concentration dependences of the permittivity ε and the orientation polarization P_{orient} were plotted and analyzed.[22] The permittivities of solutions were determined on a setup composed of a beat-frequency E12-I instrument and a temperature-controlled capacitor as a measuring cell. Refractive indices were measured with an IRF-23 refractometer.

Spectral and dynamic NMR parameters (chemical shifts and relaxation times) are known to change dramatically upon structural rearrangements in surfactant solutions;[23] this is used to determine the phase transition points (CMC).[19] Using a high-resolution Fourier-transform NMR technique with a pulsed magnetic field gradient (HR PFG FT-NMR), one can measure the diffusion coefficient D_i of each component of a solution in multi-component systems (*e.g.*, surfactant and solvent molecules).[20] The translational mobility of surfactant molecules in micelles differs from that in solution; therefore, a change in the diffusion coefficient can indicate micelle formation. The radii of diffusing molecules are calculable from their D_i values by the Stokes—Einstein equation (1)

$$D = kT/6\pi\eta R, \quad (1)$$

where η is the dynamic viscosity of the solvent, k is the Boltzmann constant, and T is the absolute temperature.

Meanwhile, the dynamic viscosity can be eliminated from the calculations by comparing the diffusion coefficients of the different components of a solution, *e.g.*, CTAB (D_{CTAB}) and water (D_{H_2O}). Then, the radii of diffusing species[20] (*e.g.*, the radius of CTAB molecules or CTAB micelles, in which CTAB molecules diffuse) can be expressed by the formula:

$$R_{CTAB} = R_{H_2O}D_{H_2O}/D_{CTAB}, \quad (2)$$

where R_{H_2O} is the water molecule radius taken to be 1.42 Å for our calculations.[24]

Diffusion coefficients D_i were measured by the PFG FT-NMR method on a modified Tesla-BS-567A NMR spectrometer (^{1}H, 100 MHz); diffusion measurements were carried out at 30 °C. Deuterated water and DMF were used in solution preparation. The D_i values of the solvents were determined from the signals of residual protons. A change in the coefficient D_i of CTAB upon the addition of AMC or AMP was indicative of mixed micellization. The coefficients D_i of AMC and AMP were not measured because the analytically significant NMR spectral lines of these compounds were hidden by the more intense lines of CTAB. The error of D_i measurements was 5—7%; the error of CMC determination, which depends on the accuracy of preparation of solutions with specified concentrations by successive dilution and the accuracy of determination of their conductivities and permittivities, was 2—5%.

Results and Discussion

Using the tensometric method, we demonstrated[12] that hydrophobic amphiphilic AMP **1** and **2** and AMC **3** and **4** capable of forming, through their hydroxy and amino groups, intra- and intermolecular hydrogen bonds and of being ionized in polar solvents, are surfactants. Their criti-

Table 1. The CMC (mol L^{-1}) of CTAB, AMP, AMC, PAMC, CTAB—AMP, CTAB—AMC, and CTAB—PAMC in aqueous DMF at its different concentrations

Concentration of DMF (vol. %)	CMCM						
	CTAB	AMC **3**	AMP **2**	PAMC	CTAB—AMC **3**	CTAB—AMP **2**	CTAB—PAMC
0	$1\cdot10^{-3}$	—	—	$1\cdot10^{-4}$ [a]	—	—	$2\cdot10^{-4}$, $8\cdot10^{-4}$ [b]
10	$6\cdot10^{-3}$	$1\cdot10^{-4}$	$6.4\cdot10^{-4}$	$1\cdot10^{-4}$	$6\cdot10^{-5}$	$8\cdot10^{-4}$	
30	$7\cdot10^{-3}$	$5\cdot10^{-5}$	$1.2\cdot10^{-3}$	$1\cdot10^{-4}$ [c]	$1\cdot10^{-4}$	$6\cdot10^{-4}$	$7\cdot10^{-4}$
40	$8\cdot10^{-3}$		—	—	$3\cdot10^{-4}$		
50	$6\cdot10^{-3}$	$7\cdot10^{-5}$	—	$6\cdot10^{-4}$	—		$8\cdot10^{-4}$
60	$6\cdot10^{-3}$		—	—	$3\cdot10^{-4}$	$8\cdot10^{-4}$	
70[c]	—	$1\cdot10^{-4}$	—	$6\cdot10^{-4}$	$2\cdot10^{-4}$		$12\cdot10^{-4}$

[a] According to the tensometric data, CMC-1 in water and aqueous 30% DMF is $2.5\cdot10^{-5}$ mol L^{-1}.
[b] For the CTAB—PAMC system in water at $C_{PAMC} = 1\cdot10^{-4}$, $4\cdot10^{-4}$, and $6\cdot10^{-4}$ mol L^{-1}, CMC-1 and CMC-2 are $2\cdot10^{-4}$, $8\cdot10^{-4}$, and $12\cdot10^{-4}$ and $8\cdot10^{-4}$, $20\cdot10^{-4}$, and $24\cdot10^{-4}$ mol L^{-1}, respectively.
[c] In DMF, the CMC of PAMC is $6\cdot10^{-4}$ mol L^{-1}.

cal aggregation concentrations (CAC) in aqueous DMF are given in Table 1.

Phosphorylated aminomethylated calixarenes (PAMC) **5** and **6** also exhibit surface activity in water and aqueous DMF, forming aggregates (see Fig. 1). Although four alkylphosphonic fragments on the lower rims of PAMC **5** and **6** could significantly affect their aggregation properties, the surface activities and CAC for AMC and PAMC were unexpectedly found to differ only slightly, being lower than the analogous characteristics of AMP and CTAB over the whole C_{DMF} range studied (see Table 1).

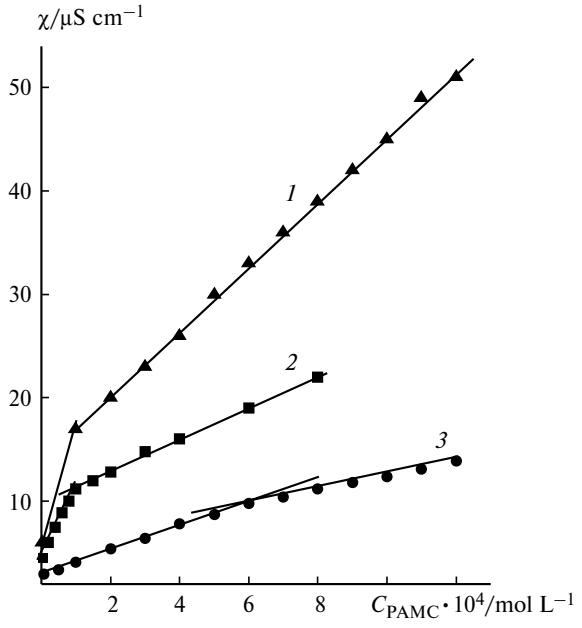

Fig. 1. Plots of the PAMC conductivity χ *vs.* the concentration of PAMC in (*1*) water, (*2*) aqueous 30 vol % DMF, and (*3*) DMF.

The CAC of PAMC **5** and **6** are equal. In acidic and neutral media, they increase from $1\cdot10^{-4}$ to $6\cdot10^{-4}$ mol L^{-1} with an increase in the DMF concentration (see Table 1). As in the case of AMC,[12] the CAC of these compounds in basic media are higher than in acidic solutions and equal to $4\cdot10^{-4}$ mol L^{-1}. Simultaneous measurements of the conductivities and pH values of PAMC solutions in the presence of an acid or an alkali for a PAMC : HCl (PAMC : NaOH) ratio of 1 : 4 showed that aggregation in the acidic and basic media is accompanied by a sharp change in pH at the CAC point (pH drops from 8 to 3.5 or increases from 8 to 10.5, respectively). This fact, as well as the aggregation of PAMC in neat DMF (in contrast to AMC and AMP) (see Fig. 1, Table 1), suggests a complex mechanism of formation of such aggregates.

In the neutral pH range, PAMC seems to be a zwitterion formed as a result of intramolecular proton transfer from acid phosphonic to basic amino groups; thus, PAMC is prepared for electrostatic aggregation. Apparently, similar to sodium calix[4]arenesulfonates[27] forming, through Na^+ cations, head-to-tail aggregates, the self-organization of PAMC proceeds *via* not only hydrophobic but also electrostatic interactions of phosphonate anions (tail) with ammonium groups (head) of different PAMC molecules in acidic and neutral media or as a result of interactions of sodium cations and phosphonate anions (tail) with the phenolate groups (head) of PAMC in the alkaline pH range. The schematic representation of electrostatic PAMC aggregation in acidic, neutral, and alkaline pH ranges is shown in Fig. 2.

Apparently, mixed aggregation in the CTAB—AMC and CTAB—PAMC systems, as well as the self-organiza-

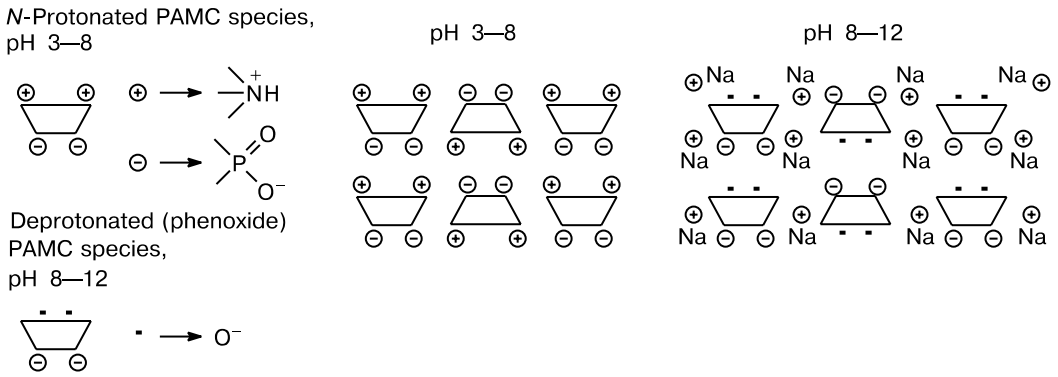

Fig. 2. Schematic representations of PAMC aggregation in acidic, neutral, and alkaline media.

tion of amphiphilic AMC and PAMC, will be driven by different main forces: hydrophobic interactions for AMC[14] and electrostatic ones for PAMC. The composition of a binary solvent can substantially affect the intermolecular interactions of solutes and their aggregation behavior.[28,29] Hence, the aggregation of AMP, AMC, and PAMC and the effect of CTAB on this process were studied at different concentrations of DMF in water (see Table 1).

To compare the micelle-forming properties of mixtures of CTAB with AMC, AMP, and PAMC and the aggregation behavior of aminomethylated compounds alone, the CMC of their solutions in water and aqueous DMF at pH 6—8 are given in Table 1. The plot of the conductivity of CTAB *vs.* its concentration in the presence of different PAMC concentrations is illustrated in Fig. 3.

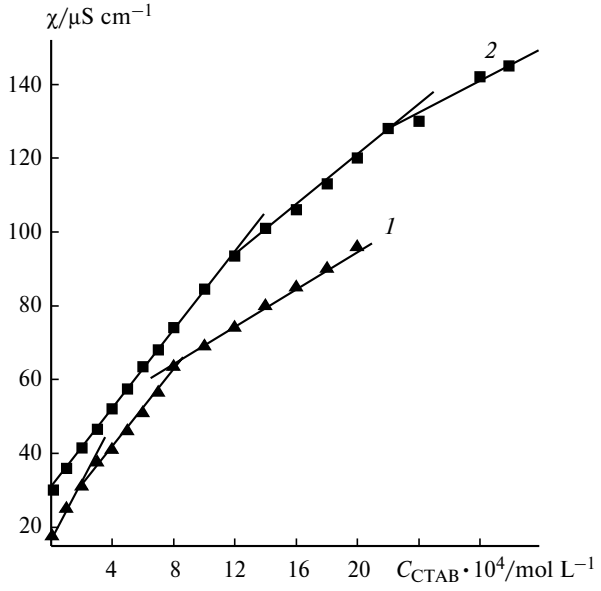

Fig. 3. Plots of the conductivity χ *vs.* the concentration of CTAB for its aqueous solutions at C_{PAMC} = (*1*) $1 \cdot 10^{-4}$ and (*2*) $6 \cdot 10^{-4}$ mol L^{-1}.

According to the data in Table 1, AMP **2** forms aggregates only in aqueous 10—30 vol % DMF, AMC **3** in the range from 10 to 70 vol % DMF, while PAMC aggregates in water, DMF, and aqueous DMF. A comparison of the CMC of the typical cationic surfactant CTAB with those of AMC and PAMC reveals the strong tendency of the latter compounds toward self-organization: the CMC of macrocyclic phenols AMC **3** and PAMC ($5 \cdot 10^{-5}$—$1 \cdot 10^{-4}$ and $1 \cdot 10^{-4}$—$6 \cdot 10^{-4}$ mol L^{-1}, respectively) is appreciably lower than the those of CTAB varying from $1 \cdot 10^{-3}$ to $8 \cdot 10^{-3}$ mol L^{-1} with the DMF content. Lower CMC ($1 \cdot 10^{-4}$—$5 \cdot 10^{-6}$ mol L^{-1}) are known[28] to be characteristic of amphiphilic macrocyclic compounds.

The dependence of the CMC of CTAB on the DMF concentration in the range from 0 to 70 vol. % shows a maximum at C_{DMF} ~40%, similarly to the viscosity changes in the water—DMF system.[26] Like urea, DMF is an organic additive that increases the CMC of ionic surfactants in aqueous solutions by changing the hydrogen-bonded water structure.[27] In binary media, the CMC of PAMC increases with an increase in C_{DMF} (*i.e.*, with an increase in the viscosity and "structuration" of aqueous DMF), while the CMC of AMC **3** slightly decreases. This can suggest that zwitterionic AMC aggregates are stabilized by involving DMF molecules, as in micelles of nonionic surfactants.[27]

In the presence of AMP, PAMC, and especially AMC, the CMC of CTAB decreases in all the mixed solvents under study (see Table 1).

An increase in C_{DMF} hinders the mixed aggregation of CTAB with methylated calix[4]resorcinarenes and PAMC. The dependence of CMC on C_{DMF} for the mixed CTAB—AMC system is analogous to that for CTAB (maximum appears at $C_{DMF} \approx 40\%$) but radically differs from that for AMC showing a minimum in the same range of DMF concentrations. Thus, the behavior of the mixed CTAB—AMC micellar system in aqueous DMF is entirely determined by the behavior of the cationic surfactant CTAB.

A peculiar behavior of the CTAB—PAMC systems in water at different PAMC concentrations is worth noting (see Fig. 3, Table 1). The plots of the conductivity *vs.* the CTAB concentration show two breakpoints (CMC-1 and CMC-2), which can indicate[29] the stepwise formation of premicellar (CMC-1) and then micellar mixed aggregates (CMC-2) with an increase in the concentration of CTAB. The first breakpoint (CMC-1) at [CTAB]/[PAMC] = 2 (see Fig. 3, Table 1) can suggest their electrostatic premicellar aggregation into 2 : 1 CTAB—PAMC species that transform, with an increase in the concentration of CTAB, into mixed micelles (CMC-2). Mixed micellization of functionalized cyclodextrins containing negatively charged groups with cationic surfactants occurs analogously; the number of surfactant molecules in premicellar aggregates corresponds to the number of negatively charged groups in the cyclodextrin molecule.[4]

Aggregation of functionalized amphiphilic macrocyclic calix[4]resorcinarenes (AMC), simple phenols (AMP), and mixed CTAB—AMC and CTAB—AMP systems in aqueous DMF was investigated more thoroughly by permittivity measurements previously applied only to micellization in low-polarity solvents.[22] To study association processes for CTAB, AMC, and AMP and detect mixed CTAB—AMC and CTAB—AMP systems, we analyzed the concentration dependences of the permittivity ε and the orientation polarization P_{orient} (Tables 2, 3; Figs. 4, 5). For dilute solutions of the surfactants (C = ~10^{-5} to ~10^{-2} mol L^{-1}), the apparent P_{orient} value (*i.e.*, the integral characteristic of a mixture of surfactant molecules and their aggregates per mole of the surfactant) was calculated from experimental ε values and refractive indices n by Eq. (3), where subscripts 12 and 1 refer to the solution and the solvent, respectively.

$$P_{orient} = 3 \cdot 10^3 C^{-1} [(\varepsilon_{12} - \varepsilon_1)/(\varepsilon_1 + 2)^2 - (n_{12}^2 - n_1^2)/(n_1^2+2)] \quad (3)$$

The plots of P_{orient} *vs.* C_{CTAB} in aqueous 30% DMF for $C_3 = 0$ and $8 \cdot 10^{-5}$ mol L^{-1} are shown in Fig. 4; analogous plots for AMP **2** and CTAB in the presence of AMP **2** ($C_{AMP} = 1.2 \cdot 10^{-3}$ mol L^{-1}) are displayed in Fig. 5.

Table 2. Permittivity ε and the orientation polarization P_{orient} of AMC **3** in aqueous 30% DMF

$C_{AMC} \cdot 10^5$ /mol L^{-1}	ε	P_{orient} /cm^3 mol^{-1}
1.65	61.35	1
5	61.5	3
6.6	61.66	21
8.3	62.28	71
10	62.43	75
12.5	62.78	82

Table 3. Permittivity ε and the orientation polarization P_{orient} of CTAB in aqueous 30% DMF at different concentrations of AMC **3**

$C_{CTAB} \cdot 10^3$ /mol L^{-1}	ε at C_{AMC}/mol L^{-1}		P_{orient}/cm^3 mol^{-1} at C_{AMC}/mol L^{-1}	
	$3 \cdot 10^{-5}$	$6 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	$6 \cdot 10^{-5}$
0.2	62.2	69.5	28	31
0.4	68	63.0	126	31.5
0.6	70.6	65.8	116	55
1	85	61.8	180	2
1.65	110.4	139	235	375
2.07	121.7	160	231	376
3.1	138.7	195	198	343
4.14	154		177	
5.18	169		165	
6.21	176		147	

For CTAB solutions (see Fig. 4, curve *1*) in the concentration range from $2 \cdot 10^{-4}$ to $7 \cdot 10^{-3}$ mol L^{-1}, decreasing P_{orient} passes through an inflection at the CMC point of the system and then decreases again. The reasons for such a shape of the curve $P_{orient} = f(C_{CTAB})$ are the reduction in the number of free polar surfactant molecules and the accumulation of their less polar aggregates, whose concentration is maximum at the CMC point ($7 \cdot 10^{-3}$ mol L^{-1}).

In the presence of AMC (see Fig. 4, curve *2*), the pattern of the P_{orient} *vs.* C_{CTAB} plot is totally different: a small plateau in the initial segment (where C_{CTAB} is comparable with C_{AMC}), suggests the association of AMC molecules with monomeric CTAB species. The CAC of the

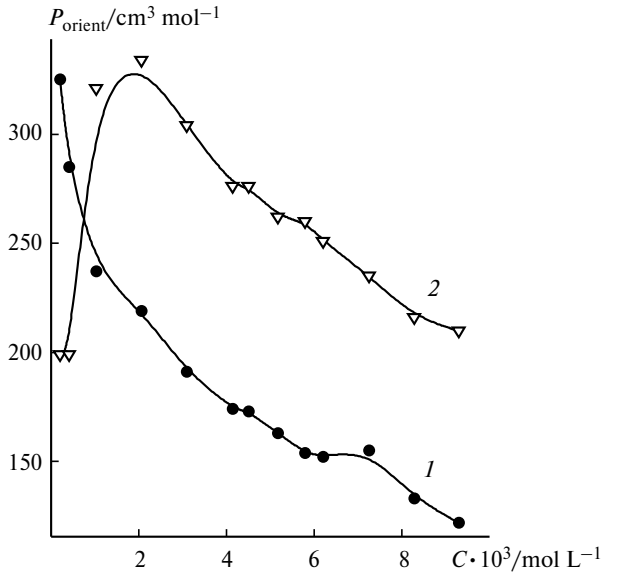

Fig. 4. Plots of the orientation polarization P_{orient} *vs.* the concentration of CTAB in aqueous 30 vol % DMF at C_3 = (*1*) 0 and (*2*) $8 \cdot 10^{-5}$ mol L^{-1}.

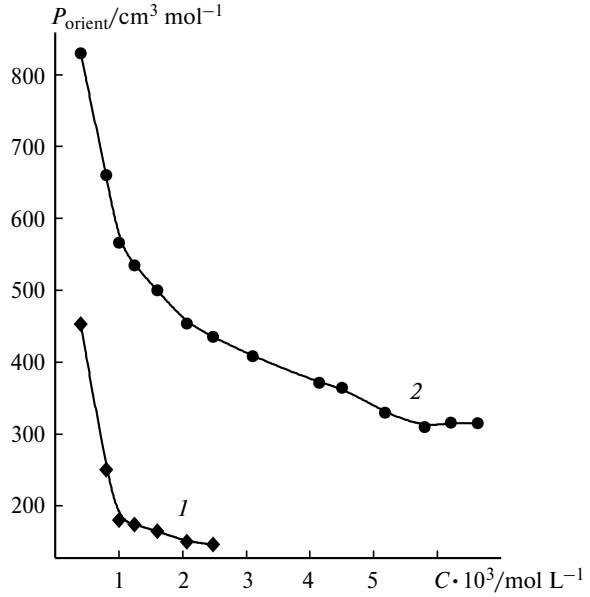

Fig. 5. Plots of the orientation polarization P_{orient} *vs.* the concentration of (*1*) AMP **2** and (*2*) CTAB in the presence of AMP **2** ($C_{AMP} = 1.2\cdot10^{-3}$ mol L^{-1}) in aqueous 30 vol % DMF.

AMC **3**—CTAB system in this segment (CAC-1) is independent of C_{AMC} (CAC-1 $\approx 3\cdot10^{-4}$ mol L^{-1} for $C_{AMC} = 3\cdot10^{-5}$, $6\cdot10^{-5}$, and $8\cdot10^{-5}$ mol L^{-1}).

Leaving the plateau, the curve $P_{orient} = f(C_{CTAB})$ steeply ascends up to a breakpoint (CAC-2) at $C_{CTAB} \approx 3\cdot10^{-3}$ mol L^{-1} and then descends gradually. Such a pattern of the plot can be interpreted as follows. A further increase in the concentration of CTAB leads to the accumulation of its polar monomeric species, which form mixed AMC—CTAB micelles at CAC-2. The subsequent decrease in P_{orient} is due to micelle thickening. The stepwise mixed aggregation of surfactants with macrocyclic compounds was noted earlier.[4,7]

To estimate the compositions of the first-step aggregates, we analyzed the dependences of the permittivity on the concentration of CTAB in the presence of AMC **3** for $C_{AMC} = 3\cdot10^{-5}$, $6\cdot10^{-5}$, and $8\cdot10^{-5}$ mol L^{-1}) in $\Delta\varepsilon$ *vs.* N coordinates, where $\Delta\varepsilon$ is the difference between the ε values for CTAB and CTAB—AMC solutions and $N = C_{CTAB}/C_{AMC}$ (Fig. 6). The curve for $C_{AMC} = 8\cdot10^{-5}$ mol L^{-1} shows a break at $N = 5$ suggesting the formation of AMC—CTAB aggregates ($\approx 1 : 5$). Similar plots with breakpoints at $N = 5$ were obtained for $C_{AMC} = 3\cdot10^{-5}$ and $6\cdot10^{-5}$ mol L^{-1}.

Qualitative analysis of $\varepsilon = f(C)$ revealed that the mixed micellization of AMC with CTAB is a two-step process: first, AMC molecules are bound (probably, through hydrophobic interactions) to monomeric CTAB species (CMC-1) and then to CTAB micelles (CMC-2).

Analogous plots of P_{orient} *vs.* C_{AMP} and $C_{AMP—CTAB}$ (see Fig. 5) show no CAC-1 point responsible for the formation of AMP—CTAB aggregates. For these systems,

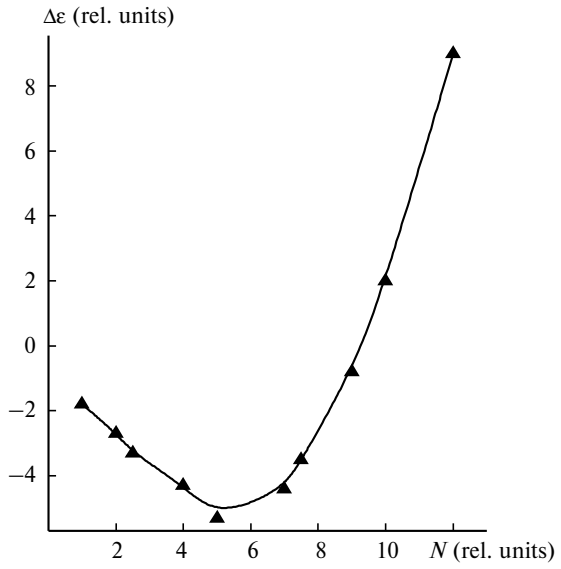

Fig. 6. Plot of the permittivity difference $\Delta\varepsilon$ between blank CTAB solutions and those containing AMC **3** *vs.* the concentration ratio N of these compounds.

an inflection point at $C = (2—4)\cdot10^{-3}$ mol L^{-1} indicates the mixed aggregation of AMP with CTAB micelles.

Thus, two types of aggregates were detected by the permittivity and conductivity measurements. At low C_{CTAB} values, hydrophobic (for AMC) or electrostatic aggregation (for PAMC) of aminomethylated calix[4]resorcinarenes with monomeric CTAB species gives 1 : 5 and 1 : 2 associates (CAC-1); at higher concentrations of CTAB, its micelles are involved in mixed aggregation (CAC-2).

The PFG FT-NMR study of the aggregation behavior of CTAB, AMC **4**, and AMP **2** in water and aqueous 30 vol % DMF revealed the effect of DMF on the CTAB micelle size; the sizes of mixed AMP—CTAB and AMC—CTAB aggregates at CAC-1 were estimated. The concentrations of AMC and AMP in the test samples, the diffusion coefficients of CTAB and water molecules, and the effective radii of the kinetic CTAB species calculated by formula (2) are given in Table 4.

Table 4. Diffusion coefficients D_i and the radii r of the kinetic species of CTAB and water in aqueous 30% DMF in the absence and in the presence of AMC **4** and AMP **2**

$C\cdot10^3$ /mol L^{-1}		$D_i\cdot10^9$ /m^2 s^{-1}		$r\cdot10^{10}$ /m
AMC **4**	AMP **2**	CTAB	Water	
—	—	0.273	1.45	7.5
0.2	—	0.178	1.25	10.0
0.4	—	0.189	1.22	9.2
0.7	—	0.201	1.28	9.0
1	—	0.134	1.06	11.2
—	3	0.193	1.31	9.6

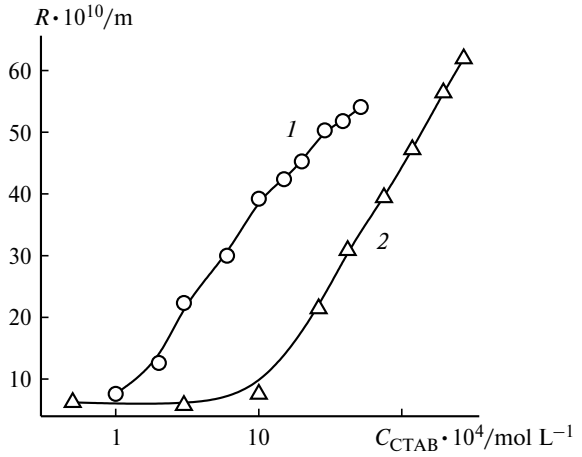

Fig. 7. Changes in the radius of the kinetic CTAB species with an increase in C_{CTAB} in (*1*) water and (*2*) aqueous 30 vol. % DMF.

The D_i measurements for water, DMF, and CTAB molecules at different C_{CTAB} values showed that an increase in the CTAB concentration only slightly affects the diffusion coefficients of water and DMF, while the D_i value of CTAB substantially decreases because of aggregation. In calculations, the apparent diffusion coefficient of the surfactant was used; the contributions of separate nonaggregated CTAB molecules to the measured diffusion coefficient were ignored. The dependences of the CTAB micelle radius calculated by formula (2) on C_{CTAB} in these systems are shown in Fig. 7. It can be seen that CTAB in water and aqueous DMF forms micelles growing with an increase in its concentration. For instance, at $C_{CTAB} = 5 \cdot 10^{-3}$ and $1 \cdot 10^{-2}$ mol L^{-1}, the hydrodynamic radii of CTAB micelles in D_2O are 23 and 40 Å, respectively; this agrees well with SANS data on the CTAB micelle sizes in water.[30,31]

The CMC point, at which the kinetic CTAB species change from individual molecules to micelles, can also be determined from the figure. The CMC of CTAB in water and aqueous DMF are $1 \cdot 10^{-3}$ and $8 \cdot 10^{-3}$ mol L^{-1}, which correlates with the conductivity and permittivity data. The radii of kinetic CTAB species in aqueous DMF at $C_{CTAB} = 1 \cdot 10^{-2}$ and $4 \cdot 10^{-2}$ mol L^{-1} are 7.5 and 32 Å, respectively (hydrodynamic radius of the CTAB molecule at infinite dilution is 7 Å).

The diffusion coefficients of the molecules of AMC **4** and DMF in aqueous DMF are $0.255 \cdot 10^{-9}$ and $1.31 \cdot 10^{-9}$ m^2 s^{-1} at $C_{AMC} = 1 \cdot 10^{-3}$ mol L^{-1} and $0.25 \cdot 10^{-9}$ and $1.23 \cdot 10^{-9}$ m^2 s^{-1} at $C_{AMC} = 7 \cdot 10^{-3}$ mol L^{-1}, respectively. The radii of the kinetic AMC species calculated by formula (2) are ~8 Å, regardless of C_{AMC}. This value is close to the size of the individual AMC molecule determined from X-ray diffraction data.[32] Therefore, AMC does not aggregate in DMF, which was confirmed by conductometric measurements.

The dependences of D_i on the increasing concentrations of AMC **4** and AMP **2** in aqueous 30% DMF at $C_{CTAB} = 1 \cdot 10^{-2}$ mol L^{-1} suggest the growth of the effective radius of the kinetic CTAB species. The radius increases from 7.5 (at $C_{AMC} = C_{AMP} = 0$) to 11 and 10 Å (at $C_{AMC} = C_{AMP} = 1 \cdot 10^{-3}$ and $3 \cdot 10^{-3}$ mol L^{-1}, respectively) (see Table 4). The conductivity measurements under analogous conditions (variable concentrations of AMC **4** and AMP **2**; $C_{CTAB} = 1 \cdot 10^{-2}$ mol L^{-1}) gave the following CMC points of mixed aggregation: $3 \cdot 10^{-4}$ mol L^{-1} for AMC and $2 \cdot 10^{-3}$ mol L^{-1} for AMP. For AMC **4**, this value equals CMC-1 determined from the conductivity and permittivity data (see Table 1), at which premicellar AMC—CTAB associates form; for AMP **2**, it is the critical concentration of the mixed micellization of AMP with CTAB. Therefore, the formation of the mixed CTAB—AMC and CTAB—AMP micelles in the water—DMF—CTAB system containing AMC and AMP is confirmed by the NMR data.

Thus, mixed micellization of amphiphilic aminomethylated calix[4]resorcinarenes and phenols with the cationic surfactant CTAB in aqueous DMF decreases the CMC and the resulting aggregates are larger than those in CTAB—DMF—water systems. The more significant decrease in the CMC for aminomethylated calix[4]resorcinarenes is due to their two-step mixed micellization with CTAB: first, with monomeric CTAB species (CMC-1) and then with CTAB micelles; micellization in the CTAB—AMP system is a single-step process. As with CTAB alone, an increase in the DMF content impedes its mixed micellization with amphiphilic phenols and calix[4]resorcinarenes. According to the data obtained, the formation of mixed micelles of macrocyclic and simple phenols with CTAB dramatically changes the properties of the system compared to solutions of individual surfactants and can substantially affect their catalytic activity. That subject will be discussed elsewhere.

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