

Receptor properties of calix[4]resorcinarenes toward tetramethylammonium and choline cations in micellar solutions of sodium dodecyl sulfate

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Concentration range of solubilization of calix[4]resorcinarene (H_8L) in sodium dodecyl sulfate (SDS) micelles was found. The interaction of the deprotonated form of H_8L (tetra-anions $[H_4L]^{4-}$) with tetramethylammonium (TMA) and choline cations in micellar solutions of SDS was studied by pH-metry and NMR spectroscopy. The concentration dependences of the change in the cloud point in a multicomponent system TMA (choline)— $[H_4L]^{4-}$ —SDS—tetrabutylammonium bromide were determined. A correlation of these dependences with host—guest binding processes was found. The sharp change in the cloud points of the corresponding micellar solutions in concentration regions of TMA ($0—5 \cdot 10^{-4}$ mol L⁻¹) and choline ($0—1.1 \cdot 10^{-3}$ mol L⁻¹) is caused by the formation of inclusion complexes TMA (choline)— $[H_4L]^{4-}$ at the interface of the aqueous and micellar pseudophases.

Key words: calix[4]resorcinarene, sodium dodecyl sulfate, extraction, solubilization, complex formation.

In recent years, micellar extraction has been intensely used in highly precision and sensitive analytical procedures of concentration, separation, and determination of both organic and inorganic ions.^{1–7} This approach is based on the solubilization of an extracted ion by micelles followed by the separation of the aqueous and micellar pseudophases. The most known method for separation are ultrafiltration⁶ and "cloud-point extraction."⁷ The name of the second procedure is associated with turbidity of transparent solutions of surfactants on heating to a certain temperature due to the separation of a surfactant solution into the micellar and aqueous pseudophases as a result of dehydration of the polar part of biphilic molecules and a decrease in their solubility in water. The introduction into the micellar pseudophase of a ionophore that can selectively bind stable ions with a high constant results in the solubilization of the latter due to binding with a receptor at the interface of the aqueous and micellar pseudophases and in a change in their composition. It is known that the cloud point (T_{cloud}) is sensitive to the nature and concentration of both ions in water^{8–11} and substances solubilized in the micellar pseudophase.¹² Therefore, it can be expected that the phenomenon of temperature-induced turbidity of a micellar solution can be applied to extraction concentrating of substrates in a separated pseudophase and also as a basis for qualitative

recognition or even quantitative determination of this or another ion in solution when using ionophores solubilized in micelles. Recognition of spectrophotometrically "transparent" organic ions, e.g., choline or its derivatives, is an urgent problem. The ability of calixarene anions to inclusion binding of organic cations^{13–15} is a prerequisite for the efficient and selective separation of the latter.¹⁶ An important characteristic of inclusion complex formation is the partial immersion of hydrophobic fragments of the substrate into the calixarene cavity, decreasing chemical shifts of protons of the substrate.¹⁷ Thus, it is of interest to study the influence of processes of inclusion binding of organic cations by calixarene-based receptors in multicomponent micellar solutions on the cloud point of the latter as a basis for the development of new analytical procedures.

According to published data,¹⁷ the deprotonated form (tetraanion) of calix[4]resorcinarene (H_8L) is an efficient receptor capable of binding tetraalkylammonium cations to form inclusion-type complexes.

We have previously^{18,19} shown that calix[4]resorcinarene (H_8L) is efficiently solubilized by micelles of non-ionic surfactants (NSurf) and dissociation of H_8L in alkaline micellar solutions is similar, to a great extent, to that in water-organic media. The dissociation of H_8L proceeds stepwise; however, the predominant deprotonated

species is the tetraanion $[H_4L]^{4-}$. The choice of the latter as a receptor solubilized in the micellar pseudophase is caused by its capability of both incorporating in micelles and selective binding in the series of tetraalkylammonium ions. According to earlier obtained data,¹⁷ in the series of the latter tetramethylammonium (TMA) is most efficiently bound by calix[4]resorcinarene anions. This fact, as well as the isostructural character of TMA and choline, whose biological significance is doubtless, predetermined the choice of the substrates.

Micellar solutions of NSurf, for instance, Triton X-100 (TX100), Triton X-405 (TX405), and Brij-35, can solubilize^{18,19} both $[H_8L]$ molecules and $[H_4L]^{4-}$ anions. Mixed micellar aggregates NSurf— $[H_4L]^{4-}$, as free $[H_4L]^{4-}$ anions, efficiently bind TMA, which does not lead, however, to a noticeable change in the cloud points. In particular, 0.02 M micellar solutions of TX100 are characterized by a low cloud point ($T_{\text{cloud}} = 54^\circ\text{C}$), which significantly increases (to 89–90 °C) upon the solubilization of the $[H_4L]^{4-}$ anions ($C = 2.0 \cdot 10^{-3}$ mol L⁻¹) by TX100 micelles but remains virtually unchanged upon the addition of TMA to the solution ($C = 2.0 \cdot 10^{-3}$ mol L⁻¹). However, if an equimolar amount of TMA ($C = 2.0 \cdot 10^{-3}$ mol L⁻¹) is added to a solution containing mixed micellar aggregates NSurf— $[H_4L]^{4-}$, the cloud point changes insignificantly (by 2–3 °C).

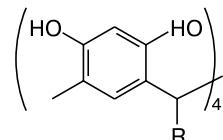
Micellar solutions of sodium dodecyl sulfate (SDS) are also known to have high solubilizing ability toward a series of organic compounds,^{20,21} including calixarenes.²² To solubilize a biphilic organic anion, its hydrophilic part is localized in the polar layer consisting of the sulfate groups of SDS, whereas the hydrophobic fragment is directed into the nonpolar core of the micelle. Unlike cyclodextrins and cucurbiturils,^{23–25} calixarenes are not characterized by inclusion of alkyl chains of surfactants into the macrocycle cavity. The hydrophobic effect, being a moving force of formation of "host—guest" complexes based on cyclodextrins, plays no noticeable role in similar compounds of calixarenes.²⁶ Intermolecular interactions between the negatively charged rim of the solubilized $[H_4L]^{4-}$ anion and sulfate groups of SDS should not either be expected. Therefore, mixed micellar aggregates $[H_4L]^{4-}$ —SDS should have good inclusion properties toward organic cations. Micellar solutions of SDS have high cloud point, which decreases in the presence of some alkylammonium salts. In particular, substitution of sodium ions for tetrabutylammonium (TBA) ions decreases the cloud point by 30–25 °C.⁹

The purpose of this work is to develop a procedure for recognition of TMA and choline cations by a change in the cloud point in a multicomponent micellar system SDS—TBA— $[H_4L]^{4-}$. To solve this problem, it was necessary to select concentration range of the solubilization of the $[H_4L]^{4-}$ ionophore and SDS micelle, study the interaction of TMA and choline with $[H_4L]^{4-}$ in micellar

solutions of SDS, and reveal regularities of changing T_{cloud} in a TMA (choline)— $[H_4L]^{4-}$ —SDS—TBA system with variation of the concentration of its components.

Experimental

Calix[4]resorcinarenes **1**–**6** were synthesized by a previously described procedure.²⁷



$R = \text{Me}$ (**1**), Pr (**2**), C_5H_{11} (**3**), C_7H_{15} (**4**), C_9H_{19} (**5**), $\text{C}_{11}\text{H}_{23}$ (**6**)

Sodium dodecyl sulfate (SDS) $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$ (Ultra Pure, >99%) purchased from MP Biomedicals, tetramethylammonium bromide (TMA) $\text{N}(\text{CH}_3)_4\text{Br}$ (98%, Lancaster), and choline chloride (high-purity grade, Chemapol) were used as received. Tetra-*n*-butylammonium bromide (98%, Lancaster) served as supporting salt.

The starting solutions were prepared by the volumetric method followed by dilution with bidistilled water.

An amount of SDS necessary for the preparation of a $2.0 \cdot 10^{-3}$ M solution of compounds **1**–**3** was determined by the successive introduction of small amounts of an aqueous solution of SDS ($C = 1.4 \cdot 10^{-1}$ mol L⁻¹) into a water—calix[4]resorcinarene system at 25 °C until calix[4]resorcinarene dissolved completely. The solubilization capacity of micellar solutions was calculated by the simplified formula^{19,28}

$$S = C_2/C_1, \quad (1)$$

where C_1 and C_2 are the SDS and solubilizate concentrations, respectively.

¹H NMR spectra were recorded on Bruker WM-400 (working frequency 400.13 MHz) and Avance-600 (working frequency 600 MHz) spectrometers.

¹H NMR-titration of TMA and choline by receptor **1** was carried out in D₂O with addition of 4 equiv. of NaOH with respect to the concentration of **1**.

pH-Metric titration of compounds **1**–**3** ($C = 2 \cdot 10^{-3}$ mol L⁻¹) in the absence and presence of TMA (choline) ($C = 2 \cdot 10^{-3}$ mol L⁻¹) was conducted in a temperature-controlled cell at 20 °C on an I-130 ionometer in aqueous solutions of SDS at the concentration of the latter $1.34 \cdot 10^{-2}$ and $3.4 \cdot 10^{-2}$ mol L⁻¹. A carbonate-free solution of NaOH ($1.65 \cdot 10^{-2}$ mol L⁻¹) was used as titrant at the same concentrations of SDS. Solutions of compound **1** in the absence and presence of TMA and choline ($3.3 \cdot 10^{-3}$ mol L⁻¹) at the SDS concentration equal to $5.06 \cdot 10^{-2}$ mol L⁻¹ were titrated at 30 °C. It is necessary to increase the temperature, because SDS is insufficiently soluble at 20 °C, which resulted in nonequilibrium conditions due to SDS cooling on the surface of the silver chloride electrode. The ionomer was calibrated by standard buffer solutions.

Mathematical processing of experimental data was performed by an earlier described procedure²⁹ using the CPESSP program.³⁰

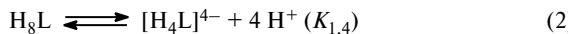
The cloud point was measured in aqueous solutions containing calix[4]resorcinarene ($5 \cdot 10^{-4}$ mol L⁻¹), SDS

($3.4 \cdot 10^{-2}$ mol L⁻¹), and TBA ($C = 10^{-2}$ mol L⁻¹), where the TMA and choline concentrations were varied within $0-8.0 \cdot 10^{-4}$ and $0-3.6 \cdot 10^{-3}$ mol L⁻¹, respectively. The solution was placed in a water bath and slowly heated to visually determined turbidity. The corresponding T_{cloud} values were determined with reproducibility ± 1 °C.

Results and Discussion

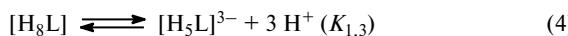
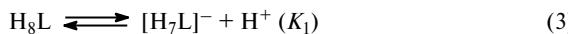
Solubilization. Derivatives of H₈L with a varied length of the hydrophobic substituent **1–6** are virtually insoluble in water but are solubilized by micellar solutions of NSurf. The solubilizing abilities of SDS and NSurf micelles toward H₈L differ substantially. Unlike NSurf, the solubilizing ability of SDS is independent of the length of the hydrophobic radical in the series **1**, **2**, and **3** ($R = \text{Me, Pr, C}_5\text{H}_{11}$) but decreases sharply with its further elongation ($R = \text{C}_6\text{H}_{13}, \text{C}_7\text{H}_{15}, \text{C}_8\text{H}_{17}$). The solubilization capacity of SDS toward compounds **1–3** is 0.15 ± 0.01 . More hydrophobic derivatives **4–6** cannot be dissolved in micellar solutions of SDS in the region of SDS concentrations used ($10^{-2}-10^{-1}$ mol L⁻¹).

"Host–guest" binding. The appearance of four charges on the rim of the cup-like ionophore H₈L, taking into account its dissociation according to the equilibrium



results in the efficient binding of the TMA cation due to noncovalent cooperative "host–guest" interactions among which electrostatic interactions prevail.¹⁷

According to the data of pH-metric titration, in micellar SDS solutions H₈L dissociates with elimination of one, three, and four protons *via* Eqs (2)–(4).



When the SDS content increases from $1.34 \cdot 10^{-2}$ to $3.4 \cdot 10^{-2}$ mol L⁻¹, the dissociation constants of compound **1** (pK_1 , $pK_{1,3}$, and $pK_{1,4}$) differ insignificantly. An increase in the hydrophobicity of the H₈L ionophores decreases its acidity (at the SDS concentration $3.4 \cdot 10^{-2}$ mol L⁻¹) in the series **1** > **2** > **3** (Table 1).

In the presence of equimolar amounts of TMA and choline, the curves of pH-metric titration of H₈L change noticeably (Fig. 1). The corresponding binding constants of TMA with resorcinarene anions, which were obtained from the pH-metric titration data assuming 1 : 1 binding at the SDS concentrations $1.34 \cdot 10^{-2}$ and $3.4 \cdot 10^{-2}$ mol L⁻¹, are presented in Table 2. Analysis of these constants shows that TMA is bound much more efficiently than choline. The $pK_{1,n}$ and $\log \beta_{11n}$ values increase with an increase in the hydrophobicity of the ionophore in the series **1**, **2**, and **3** at an SDS concentration of 0.034 mol L⁻¹ (see Tables 1 and 2). It seems natural to assume that the

Table 1. General apparent dissociation constants $pK_{1,k \pm \delta}^a$ ($k = 1, 3, 4$) of calix[4]resorcinarenes in micellar solutions of SDS with different concentrations^b

Calix[4]-resorcinarene	$C_{\text{SDS}} \cdot 10^2$ /mol L ⁻¹	pK_1	$pK_{1,3}$	$pK_{1,4}$
1	1.34	9.87	29.23	39.04
	1.54	9.57	—	38.41
	1.70	9.40	—	38.57
	3.40	9.54	29.72	38.67
	5.06	9.75	—	39.13
	1.34	9.51	—	40.88
2	3.40	9.81	30.63	40.88
3	1.34	9.72	31.35	—
	3.40	9.73	31.3	—

^a $0.03 < \delta < 0.1$.

^b At the complex content less than 10%, no correct estimation of pK is possible.

elongation of the hydrophobic radical in the series **1**, **2**, and **3** results in a deeper immersion into the nonpolar core of the micelle. Thus induced more prolong retention in the micellar aggregate is a reason for an increase in the apparent binding constant of TMA. At the same time, the most efficient binding of choline is observed for **1**, and the corresponding constants even decrease on going from **2** to **3**. Thus, choline (more hydrophilic than TMA) is predominantly bound by the most hydrophilic ionophore **1**, which is less deeply immersed into the micellar aggregate than **2** and **3**.

According to the NMR-titration data,³¹ the binding constant and also the structure of the formed complex can be evaluated in a substrate–calixarene system. The binding constants of TMA by the resorcinarene anions were determined in the region of tetraanion predomina-

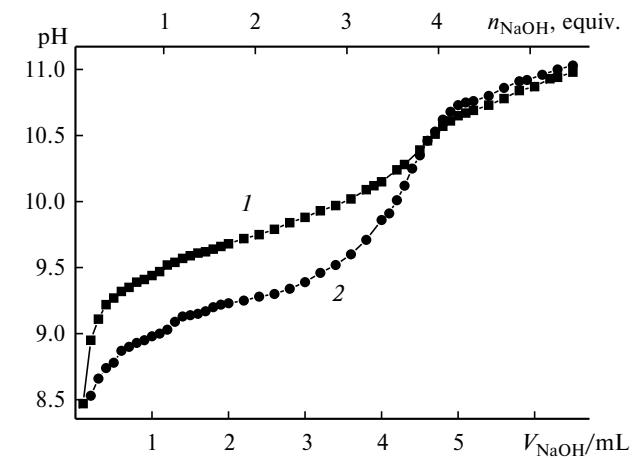


Fig. 1. Curves of pH-metric titration of compound **1** (1) and **1**–TMA system (2) in micellar solutions of SDS; $C_1 = C_{\text{TMA}} = 2 \cdot 10^{-3}$ mol L⁻¹, $C_{\text{NaOH}} = 1.65 \cdot 10^{-2}$ mol L⁻¹, $C_{\text{SDS}} = 1.34 \cdot 10^{-2}$ mol L⁻¹.

Table 2. Apparent stability constants $\log\beta_k \pm \delta^a$ of the 1 : 1 complexes of the $[\text{H}_{8-k}\text{L}]^{k-}$ anions (k is the deprotonation degree) with TMA (I) or choline (II) in 0.034 and 0.0506 M (in parentheses) micellar solutions of SDS^b

Calix[4]-resorcinarene	$\log\beta_1$		$\log\beta_3$		$\log\beta_4$	
	I	II	I	II	I	II
1	3.00 (3.00)	3.10 (2.75)	— (—)	— (—)	4.65 (4.60)	4.40 (3.93)
2	3.20 (—)	— (—)	— (—)	— (—)	5.00 (—)	3.40 (—)
3	3.52 (—)	2.52 (—)	5.25 (—)	4.25 (—)	— (—)	— (—)

^a $0.03 < \delta < 0.1$.

^b At the complex content less than 10%, no correct estimation of the stability constant is possible.

tion (fourfold excess alkali over calixarene) and at an SDS concentration of 0.05 mol L⁻¹. A necessity to use a higher surfactant concentration is related to a lower solubility of both $[\text{H}_4\text{L}]^{4-}$ and complexes formed by it in micellar solutions of SDS based on deuterated water. As follows from the NMR-titration results (Fig. 2), the signals of the methyl protons in TMA and choline undergo substantial upfield shifts with an increase in the $[\text{H}_4\text{L}]^{4-}$ concentration. The signals of the protons of the N—CH₂—CH₂OH group in choline undergo much smaller upfield shift, indicating their less preferential (compared to the N—Me fragments) immersion into the $[\text{H}_4\text{L}]^{4-}$ cavity. Even the qualitative analysis of the changes (presented in Fig. 2) in the chemical shifts of the methyl protons in TMA and choline with an increase in the $[\text{H}_4\text{L}]^{4-}$ concentration indicates that the binding of choline is more efficient

than that of TMA, which is inconsistent with the constants obtained by pH-metry. Calculation by the Benesi—Hildebrandt procedure³¹ confirms the more efficient binding of choline ($\log\beta = 3.9 \pm 0.2$) compared to that of TMA ($\log\beta = 3.2 \pm 0.2$). The obtained constants are higher than similar values found by the ¹H NMR-titration method in aqueous DMF¹⁷ ($\log\beta = 1.5$ and 1.7 for TMA and choline, respectively).

The observed discrepancy between the binding constant values obtained by pH-metry and ¹H NMR spectroscopy can be reasoned by different concentration conditions of these experiments, in particular, different SDS concentrations. Therefore, the corresponding binding constants of TMA and choline by the ionophores were determined by pH-metric titration at 30 °C under the same concentration conditions. The binding constant of TMA by the $[\text{H}_4\text{L}]^{4-}$ anion was found to remain unchanged with the SDS concentration increase from $3.4 \cdot 10^{-2}$ to $5 \cdot 10^{-2}$ mol L⁻¹ (see Table 2), while the binding constant for choline decreases and virtually coincides with a similar value obtained by ¹H NMR-titration. Thus, according to the pH-metric data, the stability constant of the $[\text{H}_4\text{L}]^{4-}$ —TMA complex is higher than the corresponding value for choline at 30 °C as well. To explain the discrepancy between the results of pH-metric and NMR-titration, one should keep in mind that the constant obtained by the first method takes into account the both types of interactions between the receptor and substrate: inclusion and non-inclusion. At the same time, the upfield shift of signals from the protons in TMA and choline with an increase in the $[\text{H}_4\text{L}]^{4-}$ concentration is a consequence of only inclusion "host—guest" complex formation.^{17,31} Therefore, the upfield shift value indicates the degree of formation of an inclusion complex. The stability constant of the TMA and choline complexes with $[\text{H}_4\text{L}]^{4-}$ obtained by the NMR method reflects the efficiency of formation of just the inclusion "host—guest" complex. Thus, the close values of choline— $[\text{H}_4\text{L}]^{4-}$ complex formation constants calculated from the pH-metric ($\log\beta = 3.93 \pm 0.03$) and NMR spectral ($\log\beta = 3.9 \pm 0.1$) data indicate the exclusively inclusion character of the complex. The higher value of the stability constant obtained for TMA by the pH-metric data is caused, most likely, by the contribution of electrostatic interactions of the non-inclusion type.

The dependence of T_{cloud} on the concentrations of the components was studied to create the optimal concentration conditions for recognition of the TMA and choline cations by the change in the cloud point in the SDS—TBA— $[\text{H}_4\text{L}]^{4-}$ micellar system. The SDS and TBA concentrations were chosen as $3.4 \cdot 10^{-2}$ and 10^{-2} mol L⁻¹, respectively, because under these concentration conditions the transition from the transparent to turbid solution is visually determined rather distinctly in a temperature range of 20—40 °C convenient for measurements. As fol-

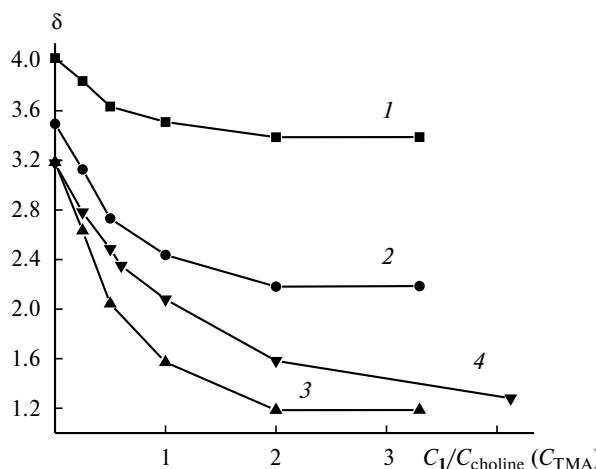


Fig. 2. Plots of the chemical shifts of the "guest" proton vs. ratio of "guest" to "host" concentrations during titration of TMA and choline with compound **1** in D₂O. Signals of choline protons: CH₂OH (1), CH₂ (2), and CH₃ (3); 4, protons of TMA.

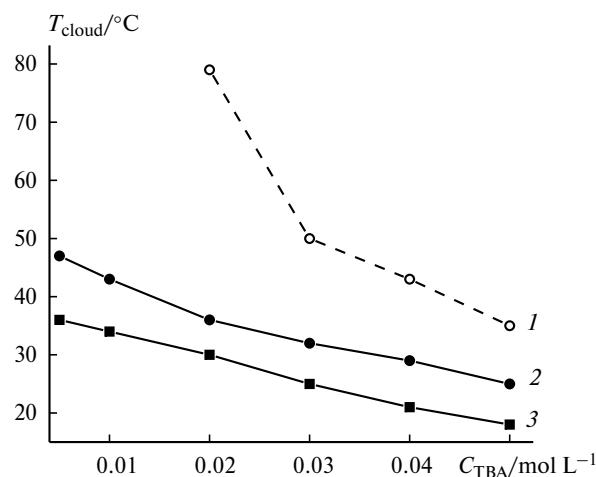


Fig. 3. Plots of T_{cloud} of solutions of SDS (1), SDS-2 (2), and SDS-3 (3) vs. TBA concentration; $C_{1-3} = 5 \cdot 10^{-4}$ mol L⁻¹, $C_{\text{SDS}} = 3.4 \cdot 10^{-2}$ mol L⁻¹.

lows from the data in Fig. 3, solubilization of $5.0 \cdot 10^{-4}$ M $[\text{H}_4\text{L}]^{4-}$ in a micellar solution of SDS is enough for a noticeable decrease in the cloud point at the same TBA concentrations. It is interesting that the corresponding cloud point values decrease in the series **3** > **2** > **1**. The cloud points for **1** under the concentration conditions studied lie below 20 °C and, hence, they were not determined.

The presence of small amounts of TMA ($5.0 \cdot 10^{-4}$ mol L⁻¹) exerts virtually no effect on the cloud point in the SDS-TBA system but noticeably changes T_{cloud} in the SDS-TBA- $[\text{H}_4\text{L}]^{4-}$ system. The dependence of the cloud point on the TMA and choline concentrations in the solution containing mixed micellar aggregates SDS- $[\text{H}_4\text{L}]^{4-}$ is illustrated in Fig. 4. The initial regions of the plots of T_{cloud} vs. concentrations of the both ions

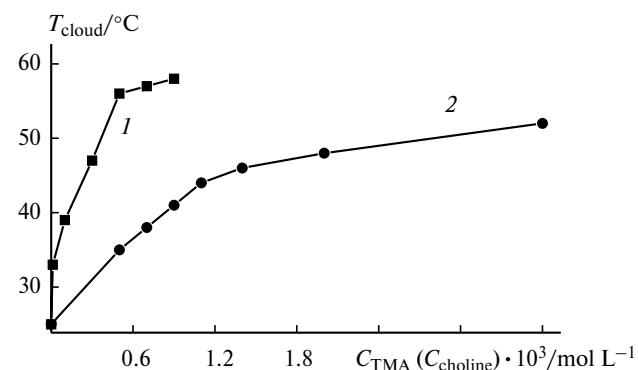


Fig. 4. Plots of T_{cloud} vs. concentrations of TMA and choline in **2**-TMA-SDS-TBA (1) and **2**-choline-SDS-TBA (2) systems; $C_2 = C_{\text{TMA}} = C_{\text{choline}} = 5 \cdot 10^{-4}$ mol L⁻¹, $C_{\text{SDS}} = 3.4 \cdot 10^{-2}$ mol L⁻¹, $C_{\text{TBA}} = 1 \cdot 10^{-2}$ mol L⁻¹.

are almost linear. However, for TMA linearity is observed in a more narrow concentration interval below $5.0 \cdot 10^{-4}$ mol L⁻¹ and characterized by a larger slope ratio than that for choline for which the linear region is finished at $1.1 \cdot 10^{-3}$ mol L⁻¹. Since the concentration of compound **2** in this experiment was $5.0 \cdot 10^{-4}$ mol L⁻¹, we can conclude that the sharp increase in T_{cloud} , which is observed with an increase in the TMA concentration to $5.0 \cdot 10^{-4}$ mol L⁻¹, indicates TMA binding at the interface of the aqueous and micellar pseudophases in this concentration interval. The further increase in the TMA concentration induces noticeably smaller changes in the cloud points, indicating the absence of further binding of TMA by the micellar pseudophase. Similar regularities were also observed for choline but the corresponding break was detected at a much higher substrate concentration. Therefore, saturation of the SDS- $[\text{H}_4\text{L}]^{4-}$ micellar aggregates occurs at higher choline concentrations, indicating that its binding is less efficient than that of TMA. Thus, the

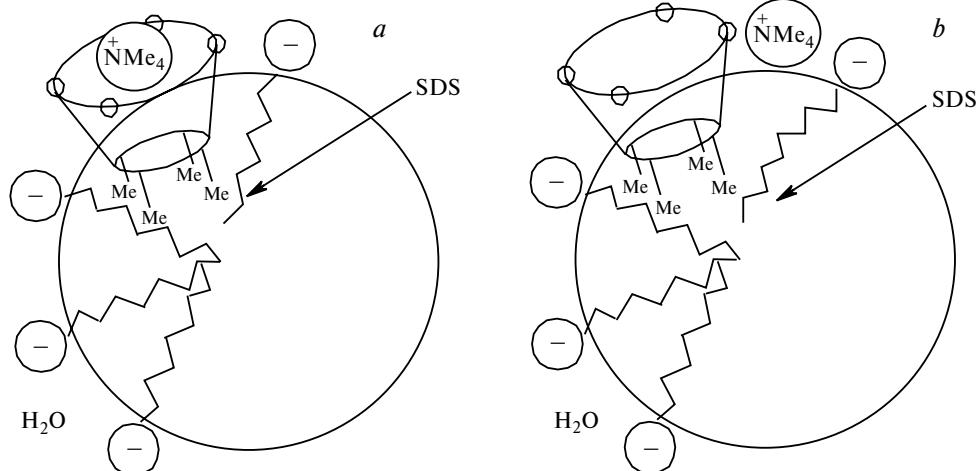


Fig. 5. Scheme of mutual "host-guest" arrangement in the complexes formed in micellar SDS aggregates for inclusion complex formation (a) and cooperative binding (b); SDS is sodium dodecyl sulfate.

regularities revealed from the dependences of the cloud points on the concentrations of the choline and TMA cations in aqueous solutions agree with the ratio of their binding constants obtained from the data of pH-metric titration but not from the data of NMR spectroscopy.

Summarizing the results, we can conclude that the solubilization of $[H_4L]^{4-}$ in SDS micelles creates conditions for efficient binding of TMA and choline cations by the micellar pseudophase. The main driving force of this binding is inclusion complex formation for which the methyl fragments of TMA and choline are immersed into the calixarene cavity, thus creating conditions for the cooperative interaction of the "guest" cation with four charges on the rim of the host (Fig. 5, a). Comparison of the pH-metric and NMR-titration data makes it possible to reveal the contribution of the electrostatic "host—guest" interactions producing no inclusion complex. It can be assumed that the efficiency of similar interaction is caused by the cooperative binding of the organic cation with the phenoxide anion at the rim of the host and the sulfate groups of SDS (Fig. 5, b).

This work was financially supported by the Russian Foundation for Basic Research (Project Nos 04-03-32909 and 05-03-08086).

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Received February 8, 2006