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Complexation and Self-Assembling of Sulfonatomethylated Calix[4]resorcinarene with Both Organic and Lanthanide Ions in Aqueous Media

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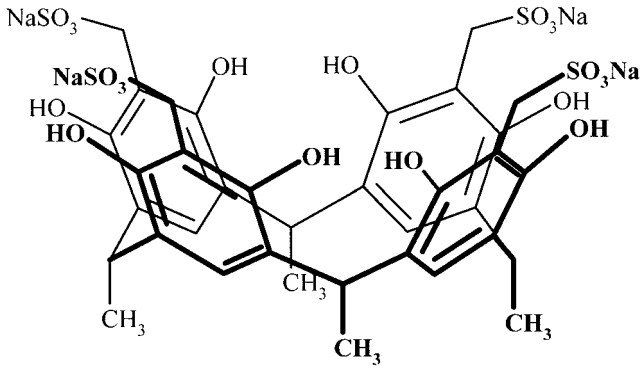
Abstract

The stoichiometry and binding constant of the paramagnetic lanthanide ion (Gd^{3+}) with sulfonatomethylated calix[4]resorcinarene (H_8XNa_4) were evaluated from the NMR relaxation data. Both ^1H NMR spectroscopy and NMR relaxation data indicate that interaction of tetramethylammonium (TEMA) and *N*-methylpyridinium (MePy) cations with H_8Xna_4 in the presence of Ln^{3+} (Lu^{3+} or Gd^{3+}) results in the formation of ternary complexes [Ln(G)H_8X] with lanthanide ions, coordinated *via* sulfonate groups and organic cation included into the cavity of H_8XNa_4. The inclusion of long-chained *N*-decyl-(DePy) and *N*-cetylpyridinium (CPy) ions into H_8XNa_4 cavity leads to self-assembling which can be revealed by NMR relaxation method with Gd^{3+} probe ions. The excess of alkylpyridinium or TEMA cations leads to disassembling of $(Gd)_n(H_8X)_m(RPy)_m$ aggregates.

Introduction

Investigation of water-soluble cyclophanes is becoming increasingly important in supramolecular chemistry, because it allows a deeper understanding of the basic forces involved in molecular recognition processes existing *in vivo* [1]. Wide application of calix[n]arenes and calix[4]resorcinarenes as artificial receptors requires new signaling systems for detection of "host–guest" complexation. From this viewpoint the application of various probing methods based on molecules and metal ions with structurally sensitive optical and magnetic properties is the best way of investigation of such systems. The qualitative detection is based on competitive interaction of guest and probe species with the host. For example, fluorescent molecules were proved to serve as probes of acetylcholine binding to calixarene [2]. Paramagnetic metal ions are known to serve as probes of aggregation in micellar systems using the ^1H NMR relaxation method [3, 4]. Thereby it was interesting to look for the possibility of an application of NMR relaxation in the presence of paramagnetic ion probes to study self-aggregation and binding in host-guest chemistry of water soluble calixarenes.



Due to dissociation of four Na^+ ions the water-soluble tetrasulfonatomethylated resorcinarene (H_8XNa_4) gives a fourfold negatively charged anion even in neutral and acidic media with hydrophobic cavity organized *via* hydrogen binding of neighboring hydroxy groups. The existence of both ionized sulfonate-groups and a hydrophobic cavity leads to H_8XNa_4 affinity towards both metal ions and organic molecules or ions. Because of this dual mode of binding it is very difficult to estimate the relative importance of electrostatic and cation-π interactions in the binding of organic cations. That is why the main goal of the work presented was to investigate interaction of water-soluble resorcinarene H_8XNa_4 with paramagnetic lanthanide ion (Gd^{3+}) as well as complex formation in the ternary systems

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H_8XNa_4-Ln^{3+}-G^+, where G^+ is a guest cation, Ln^{3+} is Lu^{3+} and Gd^{3+}. The host–guest complexation with water-soluble calixarenes is driven by electrostatic and hydrophobic interactions [5, 6]. The ratio of these two contributions is governed by the nature of the guest cation. In particular the interactions with metal ions are purely ionic, while van der Waals interactions play a significant role in the binding of alkylammonium ions [6–8]. That is why Na^+, tetramethylammonium (TEMA), *N*-methylpyridinium (MePy), *N*-decylpyridinium (DePy), and *N*-cetylpyridinium (CPy) cations were chosen as guests.

Experimental

The host H_8XNa_4 was synthesized as recently reported [9]. Salts NaCl, NH_4Cl, $Gd(NO_3)_3{\cdot}9H_2O$ and $LuCl_3{\cdot}6H_2O$ were of "chemically pure" grade (Reakhim, Russia). The commercial sample of $N(CH_3)_4Br$ was purified by recrystallization from methanol. $CH_3NC_5H_5I$ was synthesized and purified as reported [10]. "Colloid chemically pure" grade *N*-decylpyridinium and *N*-cetylpyridinium bromides were received from the Institute of Surfactants (Shebekino, Russia) and used without further purification.

Taking into account that the pH of an aqueous solution of H8XNa4 is within the range 6.0–6.5, Gd^{3+} ions should be proposed to exist partly in the form of hydroxy complexes. To avoid the effect of hydroxy complexes on the complexation between Gd^{3+} and H_8XNa_4 all experiments were run at 298 K at pH 2, maintained by required amounts of hydrochloric acid.

The 250.13-MHz ^1H NMR spectra in unbuffered D_2O were recorded at 298 K with a Bruker WM-250 spectrometer, using DSS as internal standard.

The NMR relaxation method is widely used in a study of metal-ligand and host–guest interactions in solutions [11, 12]. Since in host–guest chemistry the common NMR relaxation method procedure deals with the relaxation times of nuclei of participating species, this method fails in aqueous diluted solutions. The NMR relaxation method with paramagnetic probes uses the relaxivity of solvent molecule nuclei (e.g., protons of water molecules). The proton spin-lattice relaxation rate ($R_1 = 1/T1$) in aqueous solution containing paramagnetic probes (Gd^{3+} or Mn^{2+} ions, for example) is a sum of two main contributions – the proton relaxation rates of bulk water ($R_{1A} = 1/T_{1A} \sim 0.4$ s^{-1}, measured in the absence of paramagnetic probe) and of the water molecules in the first sphere of the metal ion ($R_{1M} = P_B/T_{1M}$, where P_B is the probability of relaxing nuclei location near the probe). The paramagnetic contribution, R_{1M}, to R_1 may be calculated by the subtraction of R_{1A} from $R1$. The relaxation rate R_{1M} changes due to variation of the number of water protons in the nearest environment of paramagnetic probe ion during complex formation [13]. Detailed expressions for the spin-lattice relaxation time are given in [14, 15].

As R_{1M} is produced by interaction between unpaired electron of metal ion and protons of coordinated water molecules, this parameter correlates linearly with the probe concentration (C_M) according to Equation (1):

$$\mathrm{MRR} = \frac{R_{1M}}{C_M}, \tag{1}$$

where MRR, M^{-1} s^{-1}, is the molar relaxation rate. Similar to molar extinction ϵ in UV-VIS spectroscopy, the molar relaxivity factor, $(MRF)_i$, characterizes intrinsic MRR values for the i-th complex ($[M(H_2O)_m]$ or any of $[M_p(H_2O)_nL_q]$). For a simple system with two sorts of metal-containing particles, M and ML, coexisting in solution (equilibrium (2)), the law of acting masses can be written as Equation (3).

$$\mathrm{M} + \mathrm{L} \rightleftharpoons \mathrm{ML}, \tag{2}$$

$$\log K_{\mathrm{ML}} = \log \frac{\alpha_{\mathrm{ML}}}{(1-\alpha_{\mathrm{ML}})} - \log \mathrm{C_L}, \tag{3}$$

where α_{ML} is the ML formation degree

$$\left(\alpha_{\mathrm{ML}} = \frac{[\mathrm{ML}]}{C_{\mathrm{M}}}\right).$$

Taking into consideration the following relationships:

$$\mathrm{C_M} = [\mathrm{M}] + [\mathrm{ML}],$$

$$\mathrm{C_L} = [\mathrm{L}] + [\mathrm{ML}],$$

where

$$[\mathrm{L}] \approx \mathrm{C_L} \gg \mathrm{C_M},$$

the α_{ML} value may be calculated from Equation (4).

$$\alpha_{\mathrm{ML}} = \frac{(\mathrm{MRF})_{\mathrm{M}} - \mathrm{MRR}}{(\mathrm{MRF})_{\mathrm{M}} - (\mathrm{MRF})_{\mathrm{ML}}}. \tag{4}$$

Any complex formation process accompanied by the change of relaxation rate can thus be easily revealed [13].

The spin-lattice (or longitudinal) relaxation times T_1 of water molecule protons were measured by the spin echo method [16] using a home-made pulse NMR spectrometer with 15.006 MHz operating frequency. The T_1 times were measured using the pulse sequence 180°-τ-90°-τ'-180° (τ = const and $\tau' \ll \tau$) [17]. The spin echo signal amplitude is determined by Equation (5):

$$A(\tau) = A[1 - 2\exp(\tau/T_1)], \tag{5}$$

wherefrom T_1 can be derived as:

$$T_1 = \tau_0/\ln 2. \tag{6}$$

Here τ_0 is an interval between pulses at $A(\tau) = 0$. The relative measurement deviation for spin lattice relaxation times does not exceed 3%.

The concentration dependencies of MRR can be mathematically treated using common procedures including computer programs (e.g., CPESSP [18]). Hence the best fit of the

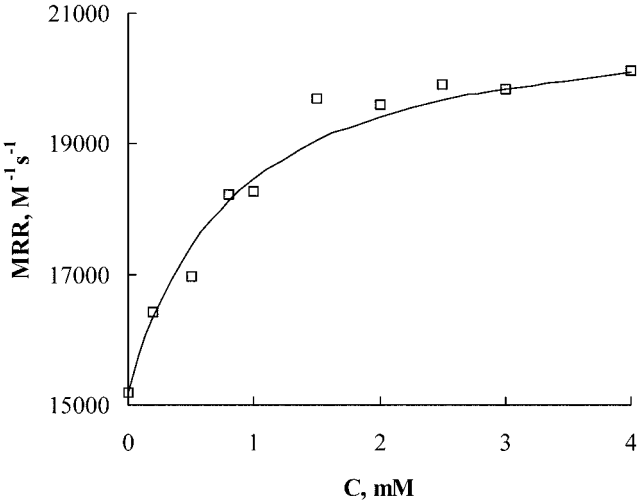

Figure 1. Plot of MRR versus H8XNa4 concentration (C) in H_8XNa_4–Gd^{3+} solutions (□). C_{Gd} = −0.1 mM; pH = 2. Solid line – MRR values calculated using log $\beta = 3.1$.

calculated MRR values might be achieved when the function F values will be minimized:

$$F = \sum_m (Q_{exp} - Q_{calc})^2 \cdot \frac{1}{\sigma^2 Q_{exp}^2}, \quad (7)$$

where Q is a characteristic parameter (molar relaxation, extinction etc.), and σ^2-dispersion. The validity of the chosen model was evaluated using transformed Fisher's criteria F_{min}:

$$F_{min} \leq F \cdot \sigma^2 (N - 2k), \quad (8)$$

where N is the total number of experiments, and k is the number of complex species. Usually about 20–25 experimental points were used to calculate complexation constants from NMR-relaxation data by means of the CPESSP program.

Results and discussion

The MRR increase from 15200 M^{-1} s^{-1} (the intrinsic MRF-value of Gd^{3+} aqueous ion) up to 20000 M^{-1} s^{-1} with H_8XNa_4 concentration (Figure 1) indicates the interaction between H_8XNa_4 and Gd^{3+}. The computer modeling of the data obtained by means of CPESSP program revealed an association with 1:1 stoichiometry

$$Ln^{3+} + H_8X^{4-} \rightleftharpoons [H_8XLn]^- \quad (9)$$

and log $\beta = 3.1 \pm 0.1$, where β is the constant of equilibrium (9) for Ln = Gd.

$$\beta = (1 - \alpha_{aq})/(\alpha_{aq}[H_8X]), \quad (10)$$

where α_{aq} is the formation degree of "free" Gd^{3+}.

The molar relaxivity factor of the resulting associate $[H_8XLn]^-$ MRF = 21000 M^{-1} s^{-1} gives the main contribution to the MRR value at more than 30-fold excess of H_8XNa_4 (Figure 1). A good fit between experimental MRR values (squares) and those calculated using $[H_8XLn]$ log β (solid line) is observed. The log β value obtained lies within the stability constant values of lanthanide complexes with sulfate ion (log β = 2.5–3.5 [19]) and *p*-sulfonatocalix[4]arene (log β = 3.8–4.2 [8]). In order to verify the Ln^{3+}-H_8X^{4-} association mode the ^1H NMR method was used with Lu^{3+} ion as a diamagnetic analogue of the Gd^{3+} ion. The lack of a down-field shift of H_8XNa_4 (C = 6 mM) in the presence of Lu^{3+} (C = 5 mM) also proves that coordination of lanthanide ions with H_8X^{4-} ion proceeds *via* the sulfonate-groups without cation-π interactions. It is naturally to predict that complexation of H_8X^{4-} with multi-charged lanthanides is tighter than with Na^+. That is why MRR of the aqueous solution containing Gd^{3+} and H_8XNa_4 slightly decreases only at high NaCl concentrations (Figure 2a) and even in 1000-fold excess of NaCl the molar relaxation rate does not reach the MRF value of Gd^{3+} aqueous ion. This indicates poor substitution of Gd^{3+} by Na^+ in such conditions. A similar behavior was found when ammonium ions were added instead of Na^+ (Figure 2a).

Due to the bulkiness and hydrophobicity of TEMA its coordination mode with water soluble calixarenes differs from that of metal ions and NH_4^+. The decrease of MRR with the increase of TEMA concentration (Figure 2a) is more pronounced than in the case of NaCl or NH_4Cl and at first glance may be produced by the competition between TEMA and Gd^{3+} according to:

$$[GdH_8X]^- + G^+ \rightleftharpoons [GH_8X]^{3-} + Gd^{3+}. \quad (11)$$

Equilibrium (11) reflects the coexistence of two processes (Equations (9) and (12)):

$$G^+ + H_8X^{4-} \rightleftharpoons [GH_8X]^{3-}. \quad (12)$$

If the above-mentioned proposal is valid, the experimentally observed MRR data presented in Figure 2a should fit the MRR-values, calculated according to Equation (13)

$$(MRR)_{cal} = (MRF)_{aq}\alpha_{aq} + (MRF)_c(1 - \alpha_{aq}), \quad (13)$$

where $(MRF)_{aq}$ and $(MRF)_c$ are the molar relaxation factors of "free" Gd^{3+} and $[GdH_8X]^-$ respectively. The α_{aq} is the formation degree of "free" Gd^{3+} ions from Equation (10) calculated by means of CPESSP program using $[H_8X]$ values from the law of acting masses (14),

$$\beta_1 = (1 - \alpha_G)/(\alpha_G[H_8X]), \quad (14)$$

where α_G is the formation degree of "free" guest (TEMA); β_1 is the constant of complexation between guest (TEMA) and H_8XNa_4 (log β_1 = 2.4 [18]).

Figure 2a demonstrates how the experimentally observed MRR-values (rhombus) differ from those (dashed line) calculated from Equation (13). This result indicates that TEMA binds without replacement of Gd^{3+}:

$$[GdH_8X]^- + G^+ \rightleftharpoons [Gd(G)H_8X]. \quad (15)$$

Thus it seems rather interesting to find out how the lanthanide ion affects on the inclusion of TEMA into

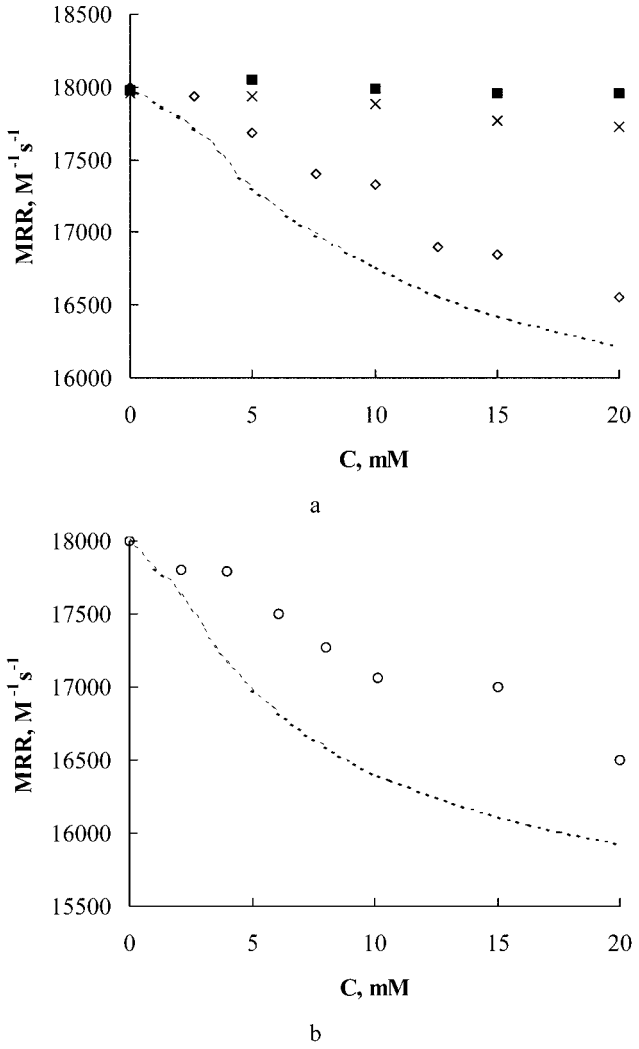

Figure 2. Plots of MRR values in solutions of H_8Xna_4–Gd^{3+}-guest versus guest concentration (C). C_{Gd} = 0.1 mM; $C_{H_8XNa_4}$ = 1 mM; pH = 2. Guests: (a) Na^+ (■), NH_4^+ (×), TEMA (◊); (b) MePy (○). Dashed lines represent theoretical predictions of MRR as a function of TEMA (a) or MePy (b) concentrations for substitution process (Equation (11)).

H_8XNa_4. The inclusion of alkyl chains of TEMA into the resorcinarene cavity results in the evident down-field shift of the H_8XNa_4 aromatic proton [20]. Therefore the NMR-titration of mixture of H_8XNa_4 and $LuCl_3$ (taken in molar ratio 1:1) by TEMA was run. Figure 3a illustrates the obtained dependence of the observed down-field shift of the aromatic protons of H_8XNa_4 ($\Delta\delta_{obs}$) on the TEMA concentration. Comparison with the data obtained from the binary H_8XNa_4–TEMA system indicates the lack of Lu^{3+} influence on the down-field shift of the aromatic protons of H_8XNa_4 in such conditions (Figure 3a). The NMR titration data of TEMA by H_8XNa_4 and H_8XNa_4:$LuCl_3$ = 1:1 blend (Figure 3b) indicate that the effect of Lu^{3+} on $\Delta\delta_{obs}$ increases with excess of $LuCl_3$ towards TEMA.

The same regularities were found in the systems MePy-H_8XNa_4-Ln on the basis of relaxation and NMR-data. The dependence of MRR on the MePy concentration (circles) (Figure 2b) also differs from the MRR values (dashed line) calculated according to the law of acting masses (Equations

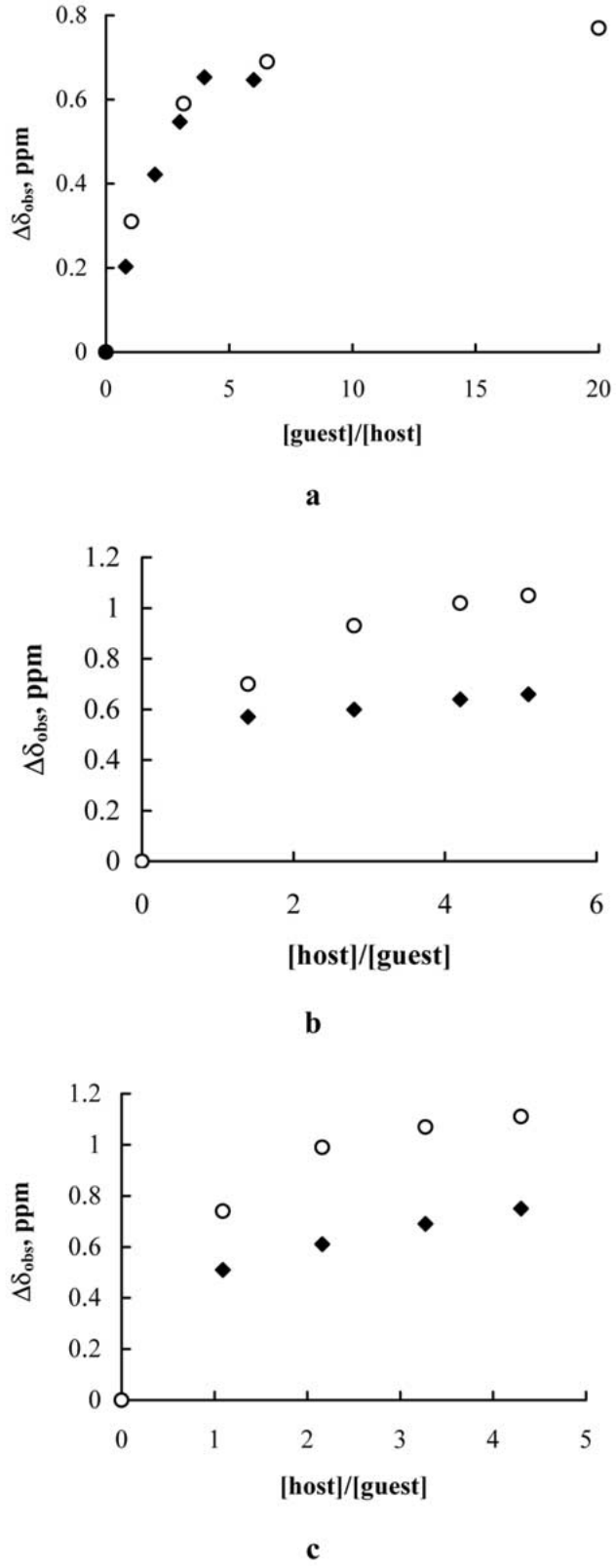

Figure 3. The plot of $\Delta\delta_{obs}$ (ppm) of H_d protons of H_8XNa_4 (a) versus [guest]/[host] with [host] = 8 mM, (○) – H_8XNa_4-TEMA, (♦) – $LuCl_3$-H_8XNa_4-TEMA, [host]/[$LuCl_3$]=1:1. The plot of $\Delta\delta_{obs}$ (ppm) of N–CH_3 protons of TEMA (b) and MePy (c) versus [host]/[guest] with [guest] = 5 mM, (○) – H_8XNa_4-G, (♦) – $LuCl_3$-H_8XNa_4-G, [host]/[LuCl3] = 1:1.

(10) and (14)) and log $\beta_1 = 2.6$ ([20]) for MePy binding to H_8X^{4-} according to equilibrium (12). Taking into account the asymmetric structure of MePy both the N-Me protons and the aromatic moiety can be incorporated into the cavity of H_8XNa_4 and thus exhibit the up-field shift. According to our previous data [20] both fragments exhibit the up-field shift under the interaction with H_8XNa_4. Unfortunately addition of excess Lu^{3+} results in a broadening of the NMR peaks of the aromatic protons. That is why only the peak of the N-Me protons can be used for monitoring MePy complexation with H_8XNa_4 in the presence of $LuCl_3$. Figure 3(c) shows the dependence of the observed up-field shift of the N-Me protons on both H_8XNa_4 and $LuCl_3$ concentrations in comparison with that in the absence of $LuCl_3$. The increase of H_8XNa_4 and $LuCl_3$ concentrations up to 6-fold excess towards TEMA or MePy results in a precipitation.

The computer modeling of the up-field shift experienced by N-CH_3 protons of TEMA and MePy under their binding with H_8XNa_4 in the ternary system (Figures 3b,c) confirms the 1:1 binding model. Thus the ^{1}H NMR-data in the ternary system (Figures 3b,c) were mathematically treated to get the binding constant between H_8XNa_4 and Lu^{3+} assuming that the displacement of TEMA or MePy ions from their complexes with H_8XNa_4 occurs according to equilibrium (16).

$$[GH_8X]^{3-} + Lu^{3+} \leftrightharpoons [LuH_8X]^{-} + G^{+}. \qquad (16)$$

According to the data obtained either Lu^{3+} forms unstable complex with H_8XNa_4 (log $\beta < 1.5$ compared to log $\beta = 3.1$ for Gd^{3+}), or Lu^{3+} binds with $[GH_8X]^{3-}$. Such binding does not prevent inclusion of TEMA (or MePy) into the H_8X^{4-} cavity thus leading to the formation of $[Lu(G)H_8X]$ complex. Taking into account the similarity of coordination properties of Gd^{3+} and Lu^{3+} and the smaller size of Lu^{3+} the first proposal seems to be invalid. Thus the obtained data can be explained by the existence of a ternary complex $[Ln(G)H_8X]$ with G^+ ion included into the cavity and Gd^{3+} or Lu^{3+} coordinated via sulfonate-groups of H_8XNa_4.

According to [21, 22] multicharged metal ions can bind two sulfonatocalix[4,5]arene anions producing capsule-type structures, when two calixarenes shroud guest due to the compensation of the electrostatic repulsion between the negatively charged calixarenes, provided by multi-charged metal ions. Shrouding of TEMA or MePy into two resorcinarene anions should result in more pronounced up-field shift and 1:2 binding model [23]. However, the data obtained (Figure 3b,c) indicate that in the ternary system the up-field shift $\Delta\delta_{obs}$ of both TEMA and MePy protons in the presence of Lu^{3+} does not exceed the $\Delta\delta_{obs}$ in the binary system and the binding model is 1:1 in both binary and ternary systems. That is why the most probable model is the binding mode found by Steed *et al.* [24] in the ternary system Na_5[p-sulfonatocalix[5]arene]-pyridine N-oxide-Gd^{3+}. According to their results lanthanide ion is bound to Na_5[p-sulfonatocalix[5]arene] *via* one of the sulfonato oxygen atoms in a bridging coordination mode with Py-N-oxide included into the calixarene cavity. So, both the NMR spectroscopy and relaxation data obtained can be explained by the existence of ternary $(Ln)_n(H_8XG)m$ complexes.

Various paramagnetic ions (e.g., Cu^{2+}, Ni^{2+}, Co^{2+}, Ti^{3+}, Dy^{3+} etc.) can be used as probes in NMR relaxation method in study of complex formation with great variety of ligands [13]. But only few metal ions (Gd^{3+}, Mn^{2+}, Fe^{3+}) can serve as probes in NMR-detection of self-aggregation phenomena. The paramagnetic relaxation time T_{1M} is a function of correlation time of proton relaxation process, τ_c,

$$\tau_c^{-1} = \tau_r^{-1} + \tau_s^{-1} + \tau_M^{-1}, \qquad (17)$$

where τ_r is a correlation time of rotation, τ_s is a correlation time of electron spin reorientation, and τ_M is a correlation time of water molecules exchange between the coordination sphere and the bulk. Since for Gd^{3+} ions the rotational correlation time, τ_r, is the shortest, the τ_r^{-1} gives the main contribution to τ_c^{-1} and paramagnetic relaxation rate R_{1M} in Gd^{3+}-solutions depends on the rotation rate of these ions. Thus when Gd^{3+} or another similar probe ion binds the charged groups in the interface of aggregates in solution (e.g., oppositely charged polymers, micelles, lipid vesicles etc.) its rotation decreases while the relaxation rate increases. This phenomenon was successfully used in NMR relaxation studies of micelle-ion association [3, 4, 25, 26] using Gd^{3+}, Mn^{2+} ions as probes. High relaxivity of Gd^{3+}-complexes with macrocyclic ligands (especially aggregated due to hydrophobic interactions) is the base of their use as contrast agents in magnetic resonance imaging [27].

Long-chained alkylpyridinium cations are known to self-aggregate in aqueous solutions. As well as the surface of their aggregates is positively charged it does not attract metal ions and NMR relaxation method with paramagnetic probes is not sensitive to aggregation of cationic surfactants. Thus rather surprising was the dramatic difference between the MRR concentration dependence for MePy (Figure 2b) and long-chained RPy (Figure 4). N-Methylpyridinium cation is known to interact with resorcinarene via both aromatic and alkyl moieties [20, 28], but the hydrocarbon chains in DePy and CPy are too bulky to be included into H_8XNa_4 cavity. That is why the incorporation into the cavity via aromatic moiety is the only binding mode for the complex formation between H_8XNa_4 and RPy. In this case the alkyl chains of RPy look outward the H_8XNa_4 cavity and can interact hydrophobically with each other. Gadolinium ions can bind the sulfonato-groups in the H_8XNa_4-Rpy associates thus producing self-assembled ternary complexes. The increase of the MRR in Figure 4 is produced by the addition of 2–3 millimoles of either CPy or DePy. Assuming that the critical micelle concentration (cmc) in pure water is 0.9 mM for cetylpyridinium bromide and near 70 mM for decylpyridinium bromide [29] the rise of MRR on Figure 4 is not governed by RPy micelles formation. That is why the growth of MRR (Figure 4) caused by the addition of long-chained alkylpyridinium ions to a solution containing Gd^{3+} and H_8XNa_4 indicates the formation of $(Gd)_n(H_8XG)m$ aggregates with high MRF values (26000–27000 M^{-1} s^{-1}).

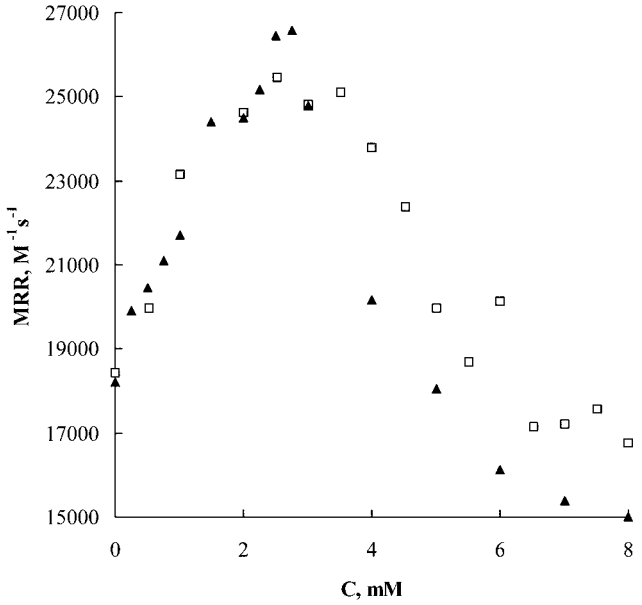

Figure 4. The plots of MRR in Gd^{3+}-H_8XNa_4-RPy systems versus alkylpyridinium ions concentration (C). RPy = DePy (□), CPy (♦). C_{Gd} = 0.1 mM; $C_{H_8XNa_4}$ = 1 mM; pH = 2.

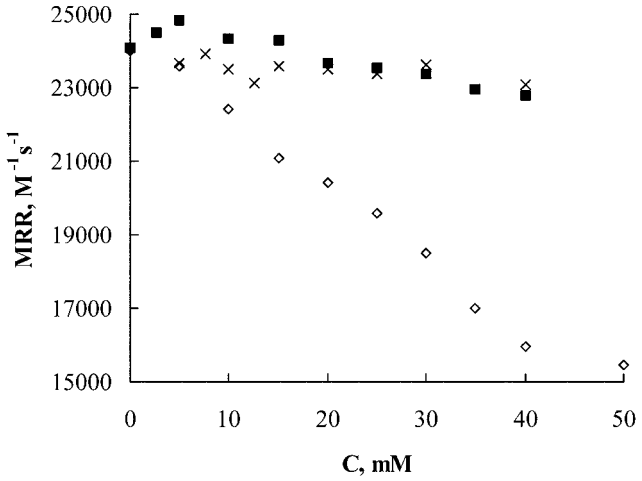

Figure 5. The effect of guest addition on MRR values in Gd^{3+}-H_8X^{4-}-$DePy^+$ solutions. CGd = 0.1 mM; CH_8XNa_4 = 1 mM; CdePy = 3 mM, pH = 2. Guests: Na^+ (■), NH_4^+ (×), TEMA (◊).

When the RPy concentration exceeds 3 mM the MRR decreases up to the Gd^{3+} MRF values (15200 M^{-1} s^{-1}) due to the replacement of gadolinium ions from $(Gd)_n(H_8X)_m(RPy)_m$ aggregates caused by resorcinarene binding with excess RPy ions (charges are omitted for clarity):

$$(Gd)_n(H_8X)_m(RPy)_m + zRPy \leftrightharpoons (H_8X)_m(RPy)_{m+z} + nGd. \quad (18)$$

Such effective interaction of pyridinium ion with sulfonato-groups is not exemplary for host–guest complexation but rather typical for counterion binding in amphiphilic systems where such electrostatic attraction of charged groups is strengthened by hydrophobic interaction of alkyl chains [30].

The results obtained indicate that Gd^{3+} can be regarded as an indicator of both the assembling and disassembling in the G^+-H_8XNa_4 system. Indeed the disassembling of the lanthanide-containing supramolecular system caused by the substitution of the long-chained alkylpyridinium guest from the assembled $(Gd)_n(H_8XDePy)_m$ complex by TEMA results in the decrease of the molar relaxation rate (Figure 5). In contrast, the addition of Na^+ or NH^{4+} ions does not influence relaxation rates (Figure 5).

Conclusions

Gadolinium ion binds sulfonatomethylated calix[4] resorcinarene H_8XNa_4 with 1:1 stoichiometry and stability constant log $\beta = 3.1$. According to ^1H NMR spectroscopy and relaxation data complexation in the ternary system Ln^{3+}-G^+-H_8XNa_4 (Ln = Gd, Lu, G^+ = TEMA, MePy) results in the complex formation with lanthanide ions coordinated via sulfonate-groups and G^+ included into the cavity of H_8XNa_4.

The self-assembling of $Gd(H_8X)G$ species (G = DePy, CPy) results in the increase of MRR, while the substitution of RPy by TEMA leads to the disassembling that is seen from the decrease of MRR. Thus the paramagnetic relaxation probe was found to be a sensitive indicator of the assembling-disassembling processes in ternary Ln^{3+}-G^+-H_8XNa_4 systems.

Acknowledgements

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