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Interactions of 3, 3.5, 4, and 4.5 generations of poly(amido amine) dendrimer with cationic surfactants

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Abstract The conductivity (κ), turbidity (τ), NMR, and Krafft temperature (T_K) studies have been carried out for hexadecylpyridinium bromide (HPyBr), hexadecylpyridinium chloride (HPyCl), and hexadecyltrimethylammonium bromide (HTAB) in the presence of 3G, 3.5G, 4G, and 4.5G generations of poly(amido amine) dendrimers (PAMAM) in aqueous phase. The cmc of all present surfactants were evaluated from κ and τ measurements, both in the presence as well as in the absence of PAMAM. The cmc values decrease in the presence of PAMAM in comparison to that in pure water, especially in the presence of amine terminated PAMAM. Krafft temperature values of pure surfactants also decrease in the presence of various generations of PAMAM. A comparison of all present results from different techniques indicates that HPyBr interacts more strongly

with all generations of PAMAM rather than HPyCl and HTAB.

Keywords Cationic surfactants · Poly(amido amine) dendrimers · Conductivity · Turbidity · NMR

Introduction

In continuation of our efforts to understand the dendrimer–surfactant interactions in aqueous phase [1–5], this study presents interactions of poly(amido amine) dendrimer (PAMAM) of generations 3G, 3.5G, 4G, and 4.5G with conventional cationic surfactants such as hexadecylpyridinium bromide (HPyBr), hexadecylpyridinium chloride (HPyCl), and hexadecyltrimethylammonium bromide (HTAB). It has been observed that

PAMAM interacts with cationic surfactants both through the non-cooperative as well as cooperative bonding [6]. The former has generally been observed at low surfactant concentration whereas the latter has been reported at higher surfactant concentration. Dendrimers are a family of polymers, which are known to form supramolecular complexes with surfactants [7–20]. It has also been reported [21] that lower generations of PAMAM undergo micelle–PAMAM complex by adsorbing themselves at the surface of micelles partially incorpo-

rating themselves in the micelles and thus stabilizing the micelles. Our previous study of the same surfactants with lower generations of PAMAM indicated clear surfactant–PAMAM complexation in the dilute surfactant concentration region [1]. Tomalia et al. [6] have suggested that there is a significant difference between the physicochemical properties of lower generations PAMAM and that of higher generations, and this shift in the properties takes place around 3.5G. The lower generations are considered to be more open for the electrostatic interactions with charged species, while the higher generations screen the inner surface groups thus providing an hydrophobic environment. The purpose of this study is to evaluate the dendrimer–surfactant interactions by using some of the higher generations of PAMAM (i.e., 3G–4.5G) and to compare the results with those of lower generations. These results have been evaluated by using various kinds of experimental techniques like conductivity, turbidity, NMR, and Krafft temperature.

Experimental

Ethylenediamine, methyl acrylate, and methanol (specially dried) were purchased from Thomas Baker, Bombay, and were used without further purification. HTAB, HPyBr, and HPyCl, all more than 99% pure from Lancaster Synthesis, England, were used as received. Double distilled water was used in the preparation of all solutions. All solutions were prepared by mass within the accuracy of ± 0.01 mg.

Poly(amido amine) dendrimers of 3G, 3.5G, 4G, and 4.5G, generations were synthesized as reported by Tomalia et al. [22] and fully characterized by IR, ^1H NMR, ^{13}C NMR, and Mass spectroscopy before use.

Conductivity and turbidity (transmittance) measurements

The conductivity measurements (κ) were carried out with the help of a digital conductivity meter model EQ 661 (Equiptronics, Bombay). The details of the conductivity measurements have been reported elsewhere [23]. Turbidity is a simple and convenient tool to detect the aggregation process, because the change in size of particles dispersed in solution is reflected sensitively in the transmittance (τ). The change in τ was measured using a Nephalo Turbidity Meter 132 (Systronics, India). The experiments were performed by adding concentrated stock solutions of each surfactant in aqueous PAMAM reference solutions by keeping the [PAMAM] constant and evaluating the micelle formation process in the presence of PAMAM dendrimers. All measurements were done at $25 \pm 0.05^\circ\text{C}$.

Krafft temperature measurements

Krafft temperatures (T_K) of HTAB, HPyBr, and HPyCl in pure water as well as in the presence of PAMAM have been carried out at $[\text{surfactant}] = 0.05 \text{ mol dm}^{-3}$. The clear aqueous solutions of each surfactant, in the presence of appropriate amounts of PAMAM, were prepared and placed in ice for at least 8 h, where the precipitation takes place. The temperature of the precipitated surfactant hydrates was raised gradually under constant stirring and its conductance was measured using a conductivity bridge EQ 661 (Equiptronics, Bombay). At each temperature, the conductance reading was checked every 2 min until it reached a steady value. The temperature was measured using a thermostatic bath (Julabo—F25) within an accuracy of $\pm 0.01^\circ\text{C}$. The

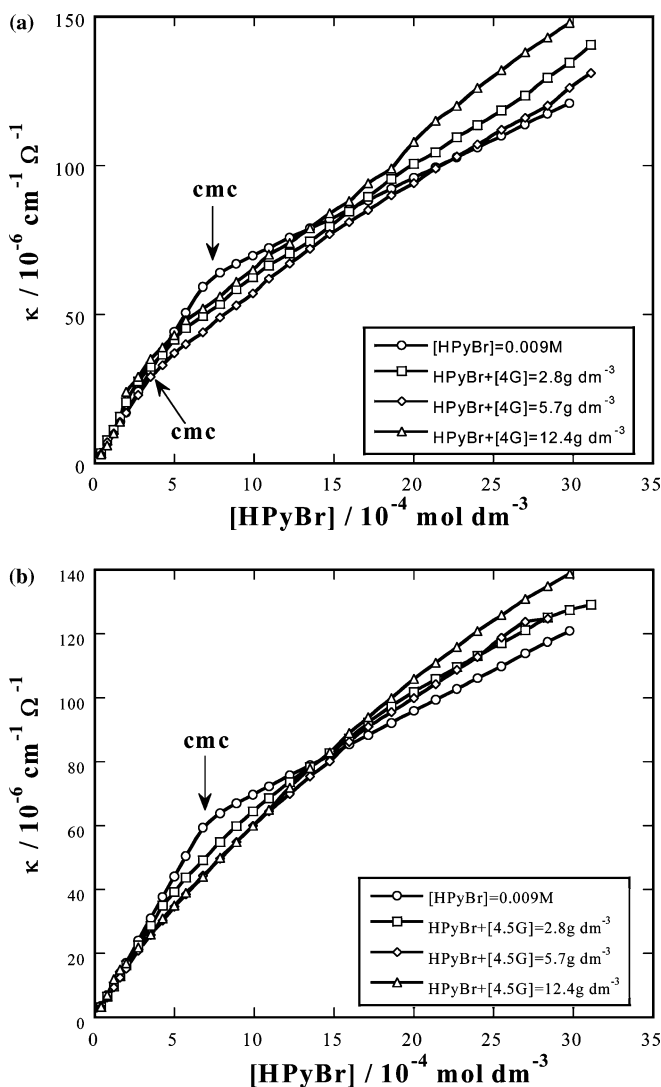


Fig. 1 a, b Plots of conductivity (κ) versus concentration of HPyBr in aqueous 4G and 4.5G PAMAM

Table 1 Values of cmc/ 10^{-4} mol dm $^{-3}$ of HTAB, HPyBr, and HPyCl in aqueous 3G–4.5G PAMAM solutions at corresponding [PAMAM]/g dm $^{-3}$ from κ and τ measurements

[PAMAM] 3G	HTAB	HPyBr	HPyCl
0.0	9.50 ± 0.01 (8.0)	7.03 ± 0.04 (6.4)	10.2 ± 0.18 (7.3)
2.8	6.32 ± 0.24 (5.2)	4.12 ± 0.21 (3.5)	6.17 ± 0.34 (6.0)
5.7	8.11 ± 0.29 (7.1)	4.11 ± 0.26 (3.8)	6.00 ± 0.33 (5.0)
12.4	7.67 ± 0.23 (7.3)	5.22 ± 0.42 (4.9)	7.64 ± 0.92 (5.2)
3.5G			
0.0	9.50 ± 0.01 (8.0)	7.03 ± 0.04 (6.4)	10.2 ± 0.18 (7.3)
2.8	9.50 ± 0.50 (7.0)	6.20 ± 0.28 (4.3)	11.6 ± 0.97 (6.0)
5.7	10.6 ± 0.50 (7.2)	6.29 ± 0.54 (4.2)	12.0 ± 0.97 (6.2)
12.4	9.88 ± 0.81 (8.0)	5.83 ± 0.31 (4.5)	7.23 ± 1.18 (6.4)
4G			
0.0	9.50 ± 0.01 (8.0)	7.03 ± 0.04 (6.4)	10.2 ± 0.18 (7.3)
2.8	6.48 ± 0.27 (6.0)	4.00 ± 0.17 (3.9)	5.58 ± 0.23 (5.4)
5.7	5.88 ± 0.17 (5.1)	5.66 ± 0.24 (4.9)	3.69 ± 0.28 (4.0)
12.4	7.67 ± 0.23 (6.2)	4.90 ± 0.21 (5.0)	4.67 ± 0.40 (4.4)
4.5G			
0.0	9.50 ± 0.01 (8.0)	7.03 ± 0.04 (6.4)	10.2 ± 0.18 (7.3)
2.8	8.96 ± 0.42 (7.0)	6.01 ± 0.15 (5.4)	11.3 ± 0.71 (7.0)
5.7	9.17 ± 0.58 (8.2)	6.41 ± 0.60 (5.6)	12.3 ± 1.03 (8.2)
12.4	12.4 ± 0.67 (8.8)	6.51 ± 1.12 (5.9)	9.33 ± 0.95 (8.8)

Values in parenthesis are from τ measurements

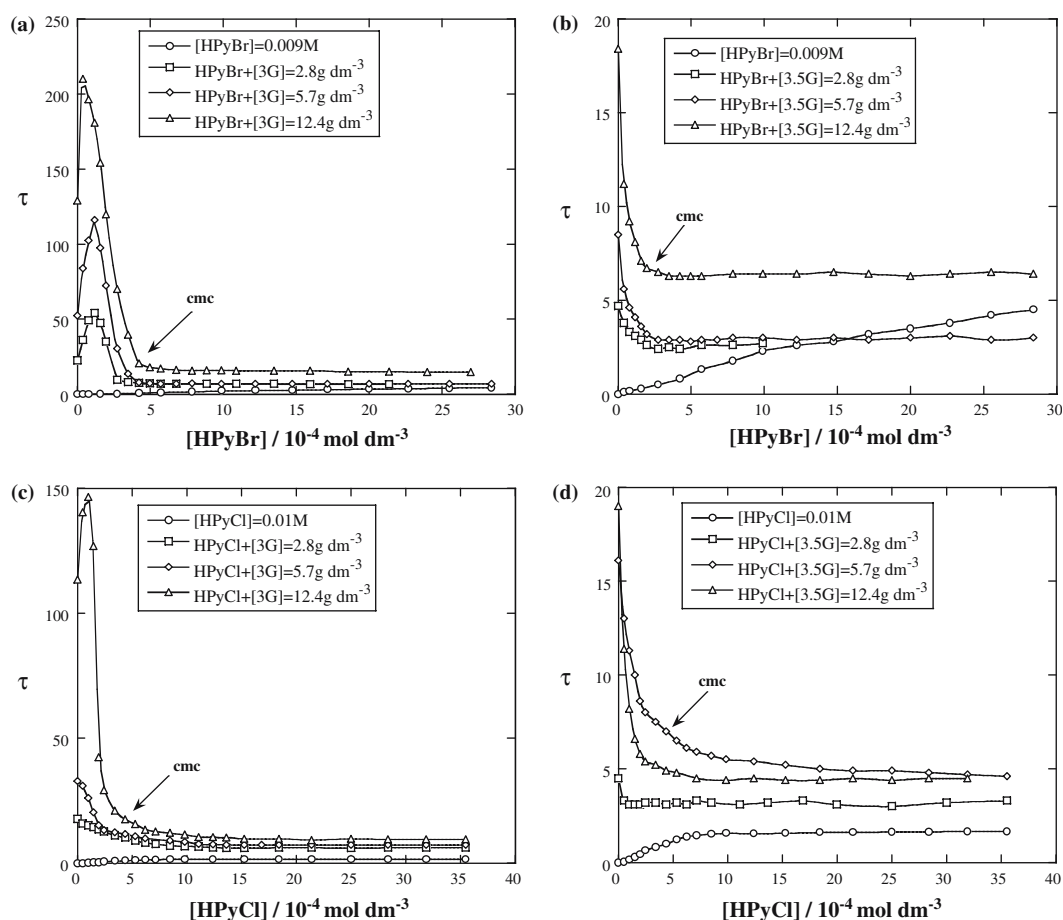


Fig. 2 a, b Plots of transmittance (τ) versus concentration of HPyBr in aqueous 3G and 3.5G PAMAM. c, d Plots of transmittance (τ) versus concentration of HPyCl in aqueous 3G and 3.5G PAMAM

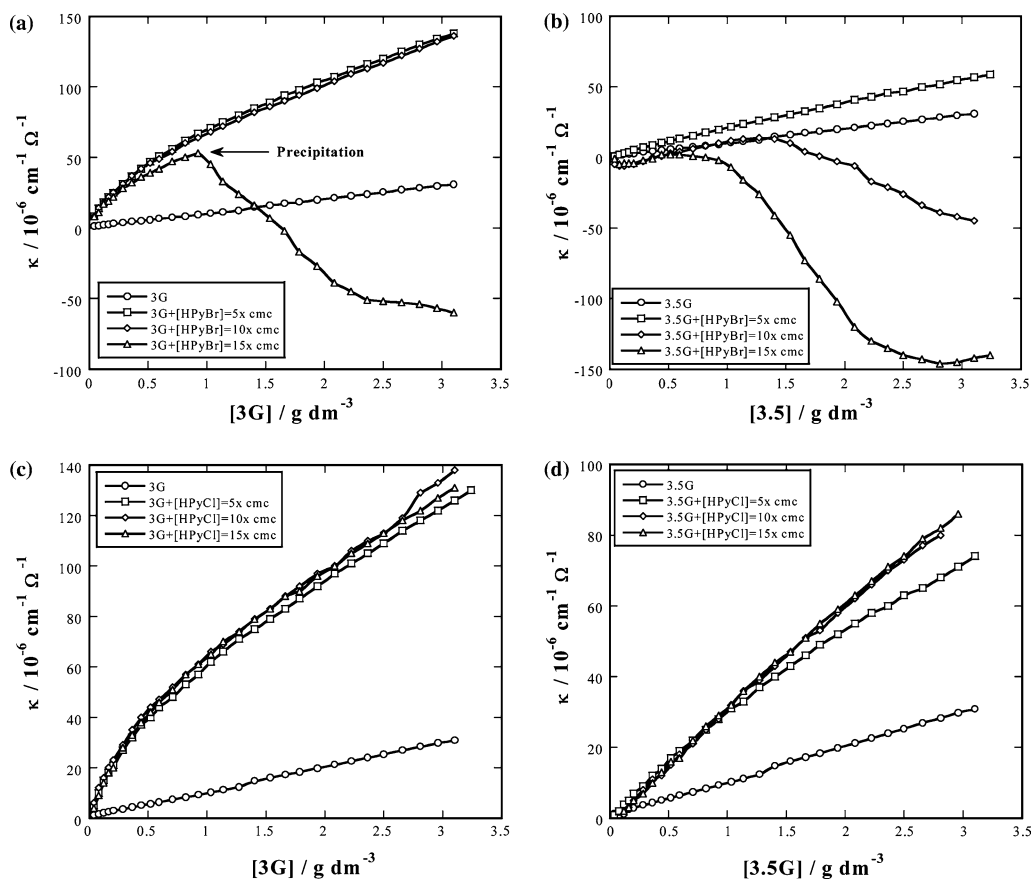


Fig. 3 a, b Plots of conductivity (κ) versus concentration of 3G and 3.5G PAMAM in the presence of different fixed concentrations of HPyBr. c, d Plots in the presence of different fixed concentrations of HPyCl

Krafft temperature was taken as the temperature where the conductance versus temperature plots showed an abrupt change in the slope [24]. This temperature was the same as that required to completely dissolve the hydrated solid surfactant.

NMR measurements

^1H NMR spectra were run on Bruker AC400E instrument. NMR measurements were carried out in D_2O and all chemical shifts were measured relative to sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS), which acted as an internal standard. D_2O , 99.9%, was purchased from Aldrich, and used as solvent.

Results

Conductivity and transmittance behaviors

Figure 1a and b show the conductivity plots of HPyBr in the presence and as well as in the absence of 4G and

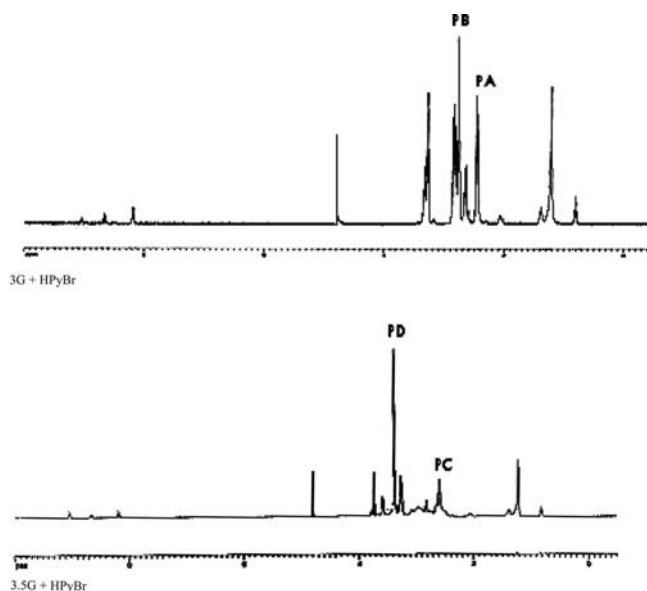
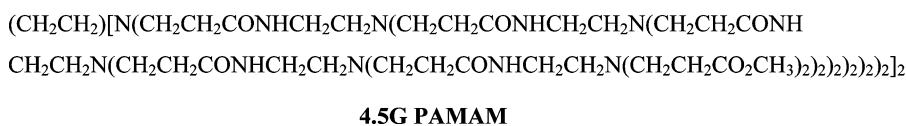
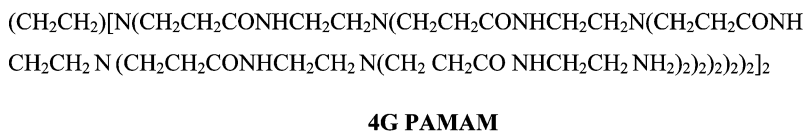
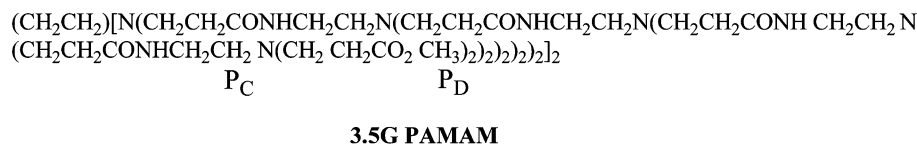
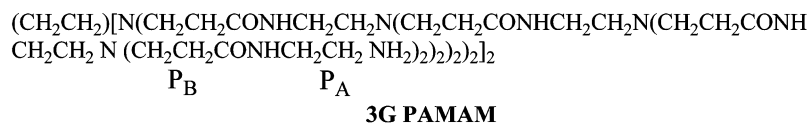


Fig. 4 Some representative NMR spectra of 3G and 3.5G PAMAM in the presence of fixed [HPyBr] also labeling protons of 3G and 3.5G PAMAM

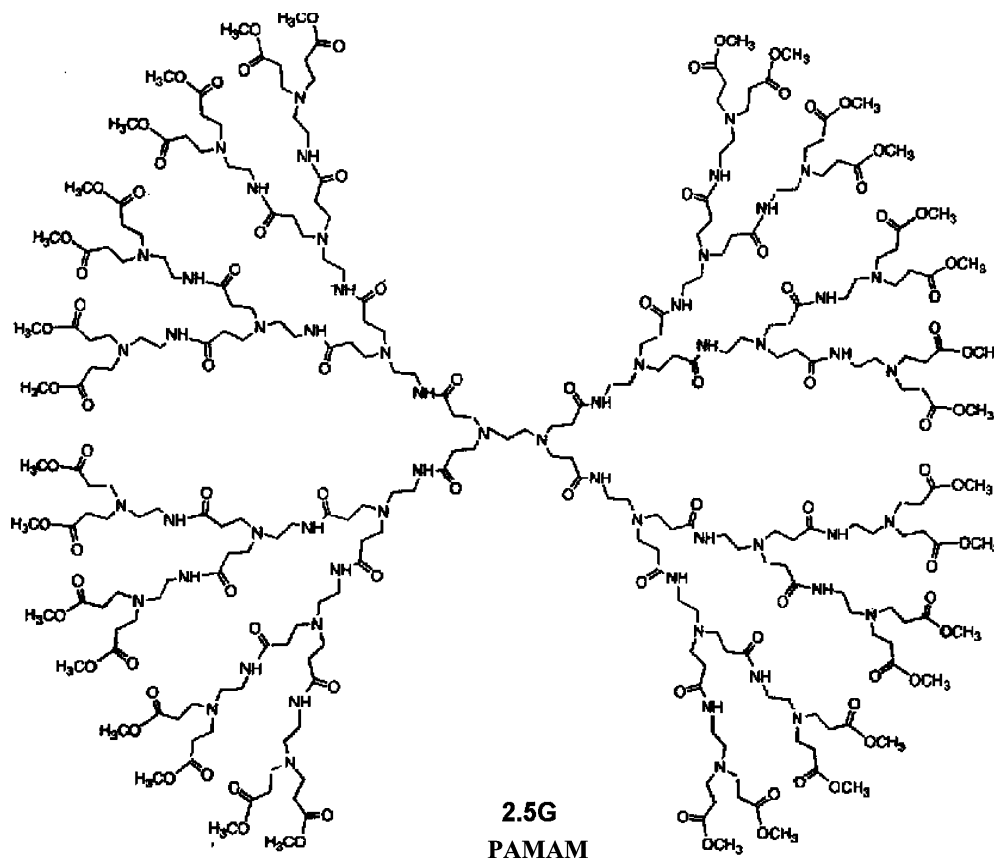
Scheme 1 Proton labeling of different protons of 3G and 3.5G PAMAM. Similar protons have also been selected for 4G and 4.5G PAMAM



4.5G PAMAM, respectively, as representative examples of κ behavior. Figure 1a shows a clear break in the κ plot of pure HPyBr and that break shifts toward the lower [HPyBr] in the presence of 4G PAMAM. However, Figure 1b does not show this behavior and instead the clear κ break of pure HPyBr converts into a shallow inflexion point in the presence of 4.5G PAMAM. A linear regression method [25, 26] was applied to calculate the cmc and their values are listed in Table 1 along with their uncertainties. A similar variation in κ has been observed for HPyBr as well as for other surfactants in other aqueous PAMAM generations (not shown). The cmc values calculated for HPyCl and HTAB have also been listed in Table 1. Figure 2 shows some representative examples of τ of HPyBr and HPyCl in aqueous PAMAM as well as in pure water. There is a contrasting difference between the τ behaviors of both surfactants in aqueous amine terminated PAMAM and in aqueous ester terminated PAMAM. Figure 2a and c demonstrates that the τ instantaneously increases with the rise in [surfactant] and after passing through a strong maximum, it falls to a constant value. The magnitude of maximum increases with the rise in the amount of dendrimer. On the other hand, no such maximum has been observed for both surfactants in aqueous 3.5G PAMAM, which is ester terminated dendritic molecule (Fig. 2b, d). In these cases, the τ value falls instantaneously with the increase in [surfactant] tending to a constant value. Apart from this, the τ is much higher in the case of Fig. 2a and c, while it is relatively very low in the case of Fig. 2b and d. A similar behavior of these surfactants as well as HTAB in other PAMAM gener-

ations has been observed (not shown). The cmc of each surfactant has been taken as that value where τ becomes constant as demonstrated in Fig. 2. It is to be mentioned here that there are several studies [27, 28] in which turbidity has been used to determine the aggregation of surfactant molecules even in the presence of polymers. These values thus calculated have also been listed in Table 1. A close inspection of all the entries in Table 1 indicates that the cmc values evaluated from both κ and τ measurements are in good agreement with each other in most of the cases. The values for all the surfactants in aqueous amine terminated (i.e., 3G and 4G) PAMAM solutions are smaller than the values in pure water. However, such values for HPyBr in aqueous ester terminated PAMAM (3.5G and 4.5G) are slightly less than that in pure water. The latter values for HTAB and HPyCl are mostly higher than the cmc in pure water. A decrease in the cmc value in the presence of PAMAM in comparison to that in pure water for a particular surfactant suggests the facilitation of micelle formation. The latter can be attributed to the favorable hydrophobic interactions among the surfactant molecules in the presence of amine terminated PAMAM which act as the driving force for the micellization. Therefore, all present surfactants demonstrate the facilitation of their micellization in amine terminated dendrimer, while this effect is weakly demonstrated by HPyBr even in the ester terminated dendrimer. This indicates that HPyBr has relatively more favorable interactions in comparison to that of HTAB and HPyCl. This is further evaluated by carrying out the κ titrations of surfactant + PAMAM solutions keeping [surfactant] constant. Figure 3 shows

Scheme 2 Structure of 2.5G PAMAM as a blue print of higher generations



the plots of κ of HPyBr and HPyCl micellar solutions with respect to the increasing amount of dendrimer keeping [surfactant] constant. Figure 3a demonstrates that the κ increases continuously with increase in the amount of PAMAM at [HPyBr] = $5 \times \text{cmc}$ and $10 \times \text{cmc}$. However, as the concentration is increased to $15 \times \text{cmc}$, the κ again increases initially but at certain [PAMAM] precipitation starts due to the insoluble salt formation (which means the neutralization of all charge sites of PAMAM) and κ starts decreasing. An analogous κ experiment of HPyCl (Fig. 3c) does not show any precipitation at [HPyCl] = $15 \times \text{cmc}$. On the other hand, precipitation occurs even at $10 \times \text{cmc}$ in Fig. 3b for HPyBr. Again no precipitation was observed for analogs in Fig. 3d for HPyCl. These results indicate that HPyBr definitely interacts strongly with PAMAM in comparison to HPyCl.

NMR and Krafft temperature behaviors

Figure 4 shows a ^1H NMR spectra of 3G and 3.5G PAMAM as representative examples showing various proton resonances labeled in Scheme 1. The structural formula of dendritic ball of 2.5G PAMAM as blue print has been given in Scheme 2. Figure 5a shows the

chemical shifts in the proton resonances of the last methylene groups in the dendritic molecules (P_A , Scheme 1) in the amine terminated 3G PAMAM. Similar proton resonances of P_B protons have been shown in Fig. 5b. A variation in the proton resonances of both protons indicates a small shielding of both P_A and P_B with respect to an increase in [HPyBr]. The upfield shift of both P_A and P_B can be attributed to the screening of their proton resonances from the magnetic field in the presence of HPyBr. On the other hand, Fig. 5c and d show the proton resonances of ester terminated PAMAM protons i.e., P_C and P_D with respect to an increase in [surfactant]. The variation in P_C and P_D proton resonances is almost identical to that of Fig. 5a and b. Here also, P_C and P_D proton resonances show mainly an upfield shift in the presence of HPyBr. All the upfield shifts of P_A , P_B , P_C , and P_D in the presence of HPyBr are of course very small but they clearly show the trend with which HPyBr interacts with PAMAM.

Figure 6a and b show the κ plots of HPyBr and HPyCl, respectively, in the presence as well as in the absence of PAMAM with respect to temperature. The T_K value has been calculated from these plots as reported elsewhere [2]. A close inspection of both figures indicates that the κ curves are quite smooth over the temperature range below the T_K in the case of HPyBr

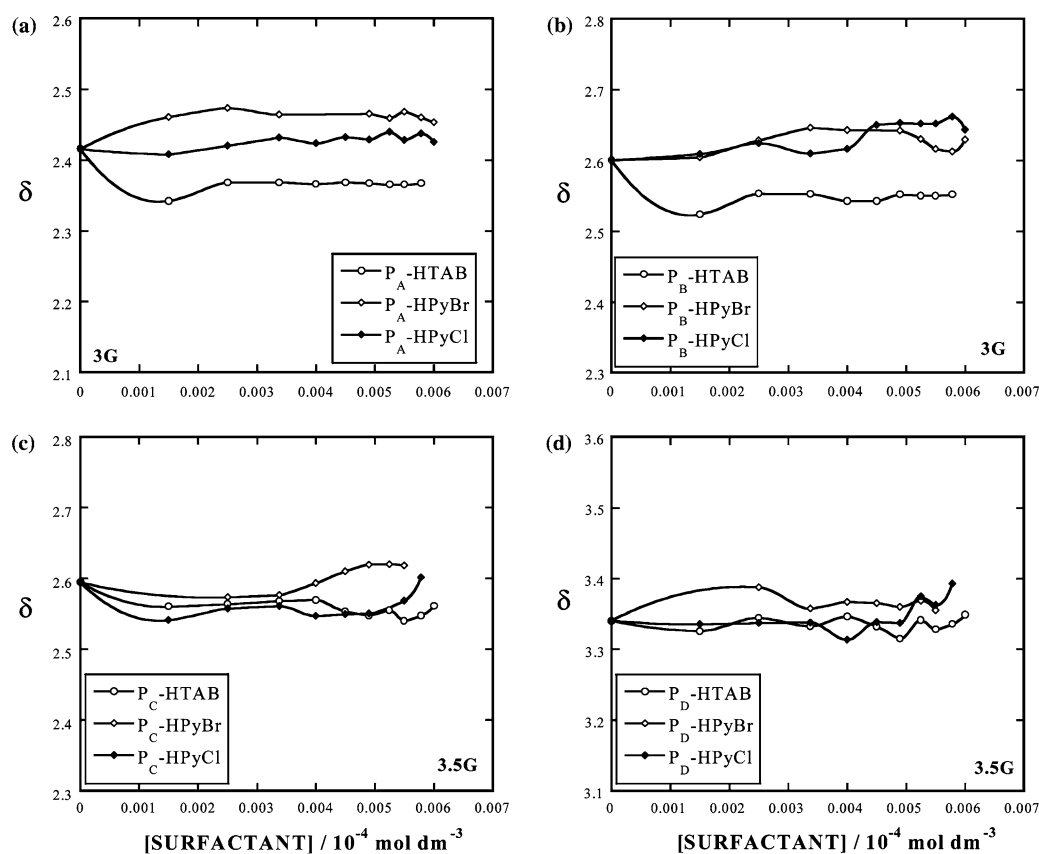


Fig. 5 a, b Plots of chemical shifts (δ) of P_A and P_B proton resonances of 3G PAMAM in the presence of HTAB, HPyBr, and HPyCl. c, d Plots of chemical shifts (δ) of P_C and P_D proton resonances of 3.5G PAMAM in the presence of HTAB, HPyBr, and HPyCl

while they are passing through a maximum in the case of HPyCl. The latter phenomenon has already been observed in HPyCl in the presence of other dendritic molecules and has been attributed to some structure transitions in the micellar phase [3]. The values of T_K have been listed in Table 2. Table 2 suggests that all values decrease with the increase in [PAMAM] and the trend is almost identical for all present surfactants. However, it is difficult to rationalize whether the additive effect of PAMAM on the T_K of HPyBr is in any way greater than HTAB and HPyCl. A decrease in the T_K value with the increase in [PAMAM] demonstrates the facilitation of solubilization of surfactant solid hydrates by aqueous PAMAM solutions and can be attributed to some favorable interactions between the two. It has been reported [29] that ionic surfactants generally interact through electrostatic interactions with PAMAM surface groups. In the present study too, the electrostatic interactions are expected to be responsible for the decrease in T_K . This has been further confirmed by determining the T_K of all present surfactants in aqueous PAMAM solutions (at fixed [PAMAM]) in the presence of salt (i.e., NaBr for HTAB and HPyBr, and NaCl for HPyCl). The T_K values computed in the presence of

different salt concentrations have been listed in Table 3. It can be seen that the increase in [salt] results in an increase in T_K value in all the cases. Thus the increase in T_K value can be related to the screening of the electrostatic interactions in the presence of salt, thereby, leading to an increase in T_K value.

Discussion

All present results from various studies indicate that HPyBr seems to have stronger interactions with the present PAMAM generations in comparison to HPyCl and HTAB. Similar results reported earlier demonstrated that HPyBr also interacts strongly with other dendritic molecules such as aliphatic and aromatic polyesters [4]. Although, all three present surfactants belong to a common category of cationic surfactants, a significant difference exists between the head group structures of HPyBr and HPyCl and that of HTAB. Apart from this, though both HPyBr and HPyCl are pyridinium cationic surfactants, the difference in their micellar properties arises from the difference in the nature of counter ions [30, 31]. It is well known that Br^-

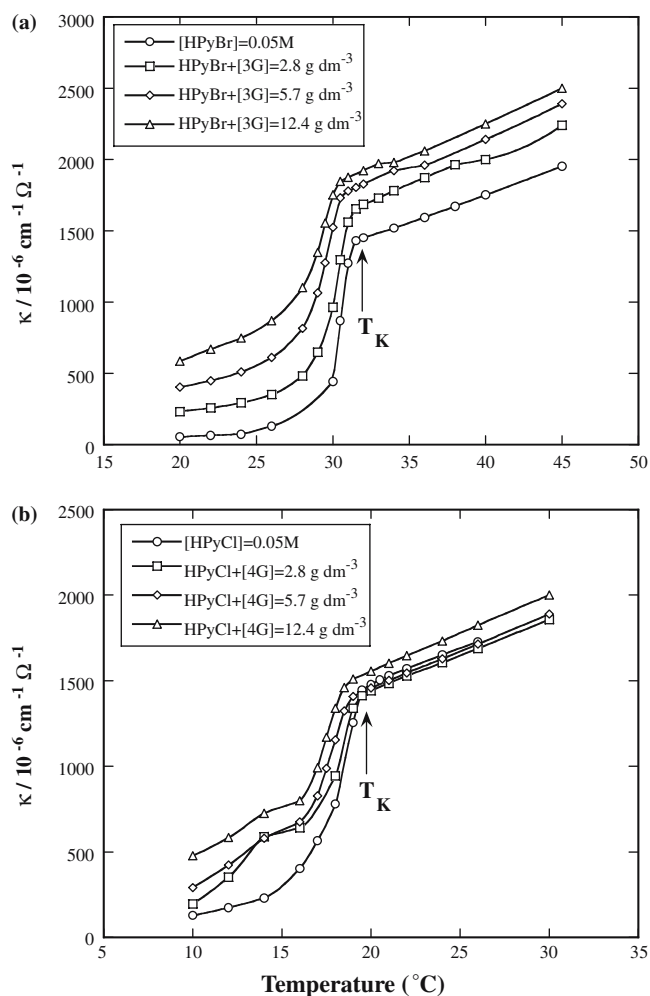


Fig. 6 Plot of conductivity (κ) versus temperature for HPyBr and HPyCl in the presence of different fixed concentrations in g dm^{-3} of 3G and 4G PAMAM respectively

counter ions are more closely associated with the micelles rather than Cl^- . A decrease in the cmc value of HPyBr in the presence of PAMAM suggests the participation of the HPyBr–PAMAM complex in the micellization process, thereby, facilitating the micellization. Though the facilitation of micellization of HTAB as well as HPyCl has also been observed especially in the presence of 3G and 4G PAMAM, no precipitation due to the insoluble salt formation of both surfactants with PAMAM has been observed as demonstrated by Fig. 3a and b for HPyBr. The NMR results further support this inference where the presence of HPyBr induces shielding of various proton resonances of PAMAM from the magnetic field (Fig. 5). This can be attributed to the adsorption of hexadecylpyridinium cation of HPyBr on the PAMAM surface due to favorable electrostatic interactions thus producing a predominantly hydrophobic complex [4]. The latter would be expected to associate favorably with the micelles of greater hydrophobicity as that of HPyBr (as shown schematically in Fig. 7). The closely bounded Br^- ions are expected to produce a strongly hydrophobic environment rather than weakly associated Cl^- ions in the case of HPyCl. As far as the comparison between the electrostatic interactions of HPyBr and HTAB is concerned, it can be said that HPyBr would generate stronger electrostatic interaction due to the presence of π electron cloud of pyridinium ring with that of weakly protonated amine or ester terminated surface groups.

As far as the comparison between the interactions of amine and ester terminated PAMAM with present surfactants is concerned, it seems that the mode of interactions in both cases is different from each other. The τ behavior supports this conclusion since there is a large difference between the τ of pure aqueous amine terminated from that of ester terminated dendrimer. A comparison between Fig. 2a and b indicates that the τ value for the former case is much higher than that in the

Table 2 Values of $T_K/^\circ\text{C}$ of HTAB, HPyBr, and HPyCl with different concentrations of 3G–4.5G in g dm^{-3}

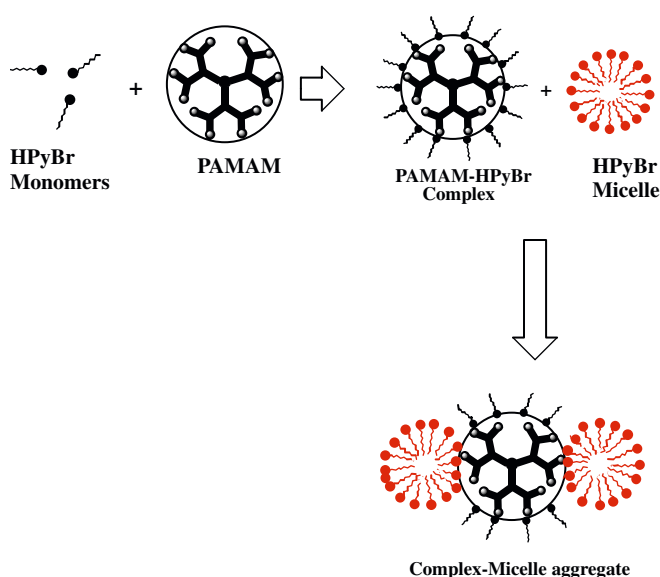
[3.0G] HTAB	T_K	[3.5G]	T_K	[4G]	T_K	[4.5G]	T_K
0.0	26.0 (25.6) ^a	0.0	26.0	0.0	26.0	0.0	26.0
2.8	25.0	2.8	25.5	2.8	25.4	2.8	25.5
5.7	24.6	5.7	24.5	5.7	25.0	5.7	25.3
12.4	24.0	12.4	24.0	12.4	24.5	12.4	24.4
HPyBr							
0.0	31.5	0.0	31.5	0.0	31.5	0.0	31.5
2.8	31.0	2.8	31.0	2.8	30.8	2.8	30.9
5.7	30.5	5.7	30.5	5.7	30.5	5.7	30.6
12.4	30.1	12.4	29.4	12.4	30.1	12.4	30.0
HPyCl							
0.0	20.0	0.0	20.0	0.0	20.0	0.0	20.0
2.8	18.8	2.8	19.0	2.8	19.1	2.8	19.0
5.7	18.4	5.7	18.0	5.7	18.6	5.7	18.5
12.4	18.0	12.4	17.0	12.4	18.4	12.4	18.0

^aReference [24]

Table 3 Values of $T_K/^\circ\text{C}$ of HTAB, HPyBr, and HPyCl with different concentrations of 3G–4.5G in g dm^{-3} in the presence of different salt concentrations (mol dm^{-3})

[Salt] ^a	[3.0G]	T_K	[3.5G]	T_K	[4G]	T_K	[4.5G]	T_K
HTAB								
0.000	0.0	24.0	0.0	24.0	0.0	24.5	0.0	24.4
0.001	2.8	25.0	2.8	25.0	2.8	24.9	2.8	24.9
0.005	5.7	26.0	5.7	25.4	5.7	25.8	5.7	25.6
0.010	12.4	26.3	12.4	26.7	12.4	27.0	12.4	26.0
HPyBr								
0.000	0.0	30.1	0.0	29.4	0.0	30.1	0.0	30.0
0.001	2.8	30.5	2.8	31.0	2.8	31.5	2.8	31.0
0.005	5.7	30.9	5.7	31.5	5.7	32.4	5.7	32.1
0.010	12.4	31.5	12.4	32.0	12.4	33.0	12.4	33.0
HPyCl								
0.000	0.0	18.0	0.0	17.0	0.0	18.4	0.0	18.0
0.001	2.8	18.5	2.8	17.5	2.8	19.1	2.8	18.7
0.005	5.7	19.3	5.7	18.3	5.7	20.0	5.7	19.5
0.010	12.4	19.9	12.4	20.0	12.4	20.7	12.4	20.2

^aNaBr has been taken for HTAB and HPyBr, while NaCl for HPyCl

**Fig. 7** A proposed schematic representation of PAMAM-HPyBr complex and its complexation with HPyBr micelle

latter case and it increases with the increase in the [PAMAM]. Since, τ value is related to the degree of scattering from the colloidal particles, therefore, higher value means higher scattering from larger particles. Hence, the amine terminated PAMAM exists in the pre-aggregated state in aqueous phase with large aggregates in comparison to ester terminated PAMAM. At high concentrations, the dendritic balls of various PAMAM generations interact with each other through a combination of both hydrophilic and hydrophobic interactions resulting in a self-aggregation. This is especially more favorable among the higher generations. It is to be mentioned here that we have tried to evaluate the size of

both the aggregates from dynamic light scattering but due to the polydisperse nature of aggregates, it was very hard to differentiate between them. Although, all present results suggest the interactions of both amine and ester terminated PAMAM with the surfactants, it is still difficult to evaluate the difference in such interactions for both dendrimers, though the interactions in both cases should be predominantly electrostatic in origin. The contrasting difference between the τ properties of Fig. 2a from that of Fig. 2b upon increase in [surfactant] can be attributed to the fact that the size of the amine terminated surfactant aggregates increases during the micellization process, while it decreases in the case of ester terminated PAMAM. This difference mainly exists in the pre-micellar region of both the figures, while there is almost comparable and constant τ value in the post micellar region. One can conclude from this behavior that the surface group difference between the present amine and ester terminated dendrimer becomes almost insignificant in the aqueous micellar solutions. That is why there is practically little difference between the chemical shifts of proton resonances both in the case of ester and amine terminated PAMAM (Fig. 5) since all NMR measurements have been carried out in micellar solutions.

Conclusion

All present surfactants interact with amine and ester terminated generations of PAMAM, but HPyBr interacts much strongly in comparison to others. The stronger interactions of HPyBr have been attributed to the stronger hydrophobic micellar environment of this surfactant due to the presence of tightly associated Br^- counter ions that facilitates the solubilization of PA-

MAM–surfactant complex. Although, a significant difference exists between the interactions of amine and ester terminated PAMAM with the present surfactants in the premicellar region, it becomes almost insignificant in the postmicellar region suggesting that the PAMAM–micelle complex remains predominantly hydrophobic in nature.

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