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Photophysical study on aggregation of carboxylic perfluoropolyether derivatives in water: Time resolved fluorescence quenching measurements in the temperature range 297–333 K

Konrad Sulak[a], Marian Wolszczak[a], Alba Chittofrati[b], Ewa Szajdzinska-Pietek[a,*]

[a] *Institute of Applied Radiation Chemistry, Technical University of Lodz, Wroblewskiego 15, 93-590 Lodz, Poland*
[b] *Solvay Solexis—Research & Technology, Physical Chemistry of Interphases, Viale Lombardia 20, 20021 Bollate (Milano), Italy*

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Abstract

Aqueous micellar solutions of fluorinated surfactants $Cl(C_3F_6O)_2CF_2COOX$, $X = NH_4^+$ or Na^+, have been examined in the temperature range 297–333 K by the time resolved fluorescence quenching technique, using cationic pyrene derivative as a luminophore and methylviologen cation as a quencher. Based on the model proposed by Infelta and Tachiya we have determined aggregation numbers, N, and rate constants of intramicellar fluorescence quenching, k_{qm}, and of the quencher exit from micelles, k^-. The observed dependencies of N as a function of temperature are compared with those reported from small angle neutron scattering studies [C.M.C. Gambi, R. Giordano, A. Chittofrati, P. Pieri, P. Baglioni, J. Texeira, J. Phys. Chem. A 107 (2003) 11558–11564; C.M.C. Gambi, R. Giordano, A. Chittofrati, P. Pieri, P.Baglioni, J. Texeira, J. Phys. Chem. B 109 (2005) 8592–8598]. The k_{qm} and k^- data, and the respective activation energies, are discussed in terms of micellar size, packing of surfactant molecules and charge density at the interface, depending on surfactant concentration and the kind of counterion.

Keywords: Perfluoropolyether surfactants; Micelles; Fluorescence quenching; Kinetics; Aggregation number

1. Introduction

Fluorescence probe methods are widely employed in the studies of self-assembled amphiphilic systems [1]. In particular, examination of fluorescence quenching of the probes embedded in micelles enables to determine micellar aggregation numbers, N. Such studies are sparse, however, for fluorinated systems because popular protiated luminophores and quenchers often appear incompatible with the host.

We have shown that aggregation numbers of anionic fluorosurfactants in aqueous solutions at room temperature can be obtained from time resolved fluorescence quenching (TRFQ) measurements using cationic luminophore: 1-pyrenebutyltrimethylammonium bromide (PBTMA), and cationic quencher: 1,1′-dimethyl-4,4′-bipyridinium dichloride (methylviologen, MV) [2]. This method, based on the model developed by Infelta and Tachiya [3,4], was recently applied to study aggregation of $Cl(C_3F_6O)_nCF_2COOX$ compounds (PFPE-n-X), consisting of $n = 2$ or 3 isopropoxy units and the counterion $X = Na^+$ or NH_4^+ [5]. A significant growth of PFPE-n-X aggregates was observed with increasing surfactant concentration. Very high aggregation numbers at large surfactant concentrations were rationalized assuming a transition from spherical to ellipsoidal micelles, in agreement with the results of small angle neutron scattering (SANS) studies [6–8]. Furthermore, it was concluded in the TRFQ study that the degree of counterion binding to micelles is higher for NH_4^+ than for Na^+; as a consequence N values at a given surfactant concentration, and the rate constants of intramicellar quenching at a given N (above $N \sim 40$), are higher for the ammonium salt.

The present work has been aimed to test usefulness of the PBTMA/MV probe pair for examining fluorinated surfactant micelles at elevated temperatures, up to 333 K. Analysis of the TRFQ data for selected PFPE-2-X systems enabled us to determine temperature effect on aggregation numbers of spherical and ellipsoidal micelles, and to estimate activation energies of

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[*] Corresponding author. Tel.: +48 42 6313189; fax: +48 42 6840043.
E-mail address: espietek@mitr.p.lodz.pl (E. Szajdzinska-Pietek).

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intramicellar fluorescence quenching and of the quencher exit from the aggregates. Some preliminary results have been presented earlier [9].

2. Materials and methods

PFPE-2-X surfactants of purity around 99% (with respect to the formula given above) were supplied by Solvay Solexis—Research & Technology, Bollate (Milano), Italy. Their synthesis and chemical analysis has been described by Tonelli et al. [10]. PBTMA (Molecular Probes) and MV (98%, Aldrich) were used as received. Water was purified using the Millipore system (Milli-Q Plus). Preparation of samples, the photolysis setup based on a nitrogen laser (Laser Photonics 120C: pulse 300 ps, 50 μJ, or PTI GL-3300: pulse 800 ps, 300 μJ) and details of TRFQ measurements have been described earlier [5,11]. Kinetic traces were recorded at selected temperatures for the surfactant solutions containing $\leq 5\,\mu\text{mol dm}^{-3}$ PBTMA (average probe/micelle ratio ≤ 0.01) and various concentrations of MV, not exceeding the micelle concentration. The samples were carefully deaerated by bubbling with argon gas (40 min at least) and equilibrated at a given temperature (measured with accuracy ±0.5 K) for at least 20 min.

3. Analysis of the kinetic traces

The results of TRFQ experiments were analyzed with the model developed by Infelta and Tachiya [3,4]. The model assumes that the intramicellar quenching is a classical first order process, and the observed nonexponential decay curves, fluorescence intensity (I) versus time (t), Eq. (1), are due to the distribution of the luminophore and quencher molecules between micelles according to Poisson statistics

$$I(t) = A_1 \exp\{-A_2 t - A_3[1 - \exp(-A_4 t)]\} \tag{1}$$

where $A_1 = I(0)$, and the parameters $A_2 - A_4$ are given by:

$$A_2 = k_0 + \frac{k^+ k_{\text{qm}}[Q]}{(1 + K[M])(k^- + k_{\text{qm}})} = k_0 + S_2[Q] \tag{2}$$

$$A_3 = \frac{k_{\text{qm}}^2[Q]}{(k^- + k_{\text{qm}})^2(1/K + [M])} = S_3[Q] \tag{3}$$

$$A_4 = k_{\text{qm}} + k^- \tag{4}$$

where k_0 is the rate constant of fluorescence decay in the absence of the quencher; k^+ and k^- are rate constants of the quencher entry to, and exit from micelles, respectively; $K = k^+/k^-$ is the equilibrium constant of the quencher binding to a micelle; k_{qm} is the pseudo-first order rate constant of intramicellar fluorescence quenching; $[Q]$ and $[M]$ are the quencher and micelle concentrations, respectively.

The above equations simplify in the case of so-called immobile quenchers, which do not migrate between micelles during the life time of the excited luminophore. Then $A_2 = k_0$ (k_0 can be determined in a separate experiment for $[Q] = 0$), $A_3 = [Q]/[M]$ (the average occupation of micelles by the quencher), $A_4 = k_{\text{qm}}$, and the concentration of micelles is given by the slope of the linear A_3 versus $[Q]$ dependence. In the case of a mobile quencher we have used an iterative procedure [12] to obtain the rate constants k^- and k_{qm}, based on Eqs. (2)–(4), and the concentration of micelles was determined under the assumption: $k^+[M] \gg k^-$. The aggregation number, N, for a given amphiphile concentration, C_a, was calculated from the relation:

$$[M] = \frac{C_\text{a} - \text{CMC}}{N} \tag{5}$$

where CMC is the critical concentration of micellization, assumed as 0.021 and 0.020 mol/dm^3 for PFPE-2-NH$_4$ and PFPE-2-Na, respectively (like in the previous fluorescence and SANS studies [5–8]), according to surface tension and conductivity data at room temperature [13,14]. We note that the recent ESR spin probe study of the PFPE-2-NH$_4$ system indicates no CMC change with temperature increase up to 333 K [15], although the ESR value is lower, CMC = 11 ± 1 mmol/dm^3. Such difference in CMC is not significant for determination of aggregation numbers at higher surfactant concentrations (cf. experimental errors below), but for the 0.048 mol/dm^3 solution of PFPE-2-NH$_4$ the N data obtained with the lower CMC value would by higher by 8–11 units (depending on temperature).

It is relevant to add that the above model assumes complete binding of the luminophore to micelles. Although PBTMA is soluble to some extent in water, such assumption is justified taking into account the very low probe/micelle concentration ratio (vide supra) and positive electrostatic interactions of PBTMA with micelles. Our complementary experiments with the use of I$^-$ anions as quenchers indicate that the amount of the free probe is indeed negligible. For the I$^-$ concentrations, which effectively quench PBTMA fluorescence in neat water, no quenching was observed in micellar solutions (in the examined range of surfactant concentration and temperature). We also note that in well-deaerated PFPE-X systems the rate constants of spontaneous fluorescence decay (k_0 values) are lower than in neat water and independent of surfactant concentration.

4. Results and discussion

We have examined three micellar systems: 0.201 mol/dm^3 PFPE-2-Na, 0.048 mol/dm^3 PFPE-2-NH$_4$ and 0.390 mol/dm^3 PFPE-2-NH$_4$. The first one has been selected to compare temperature effect on the aggregation number with that reported in the SANS study [8]. Agreement between room temperature data obtained by TRFQ and SANS is better in the case of the sodium salt as compared to the ammonium salt [5,8]. The other two systems have been examined in the present work with the aim to compare the behavior of small spherical micelles and large ellipsoidal micelles; N increase with surfactant concentration is larger for the ammonium salt [5]. In complementary experiments we have also examined temperature effect on the kinetics of PBTMA fluorescence quenching by MV in neat water.

At room temperature (297 K) the MV quencher behaves as an immobile quencher, there is no increase of A_2 parameter in Eq. (1) with the quencher concentration. The k_{qm} and N values determined in this study are in agreement with those reported in

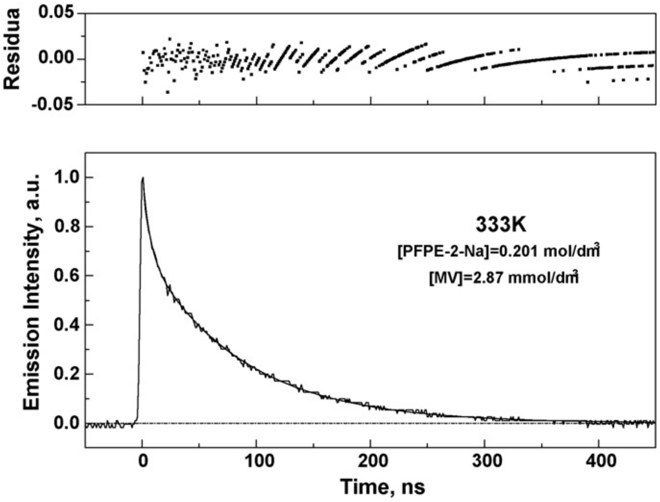

Fig. 1. An example of fluorescence decay at 333 K (emission wavelength 405 nm) in the PFPE-2-Na/PBMTA/MV system. Lower panel—noisy curve: experimental run; smooth curve: the best fit with the use of Eq. (1), where $A_2 = 11.6 \times 10^6\ s^{-1}$, $A_3 = 0.38$ and $A_4 = 13.8 \times 10^7\ s^{-1}$.

Ref. [5], within the uncertainty not higher than ±4 for N, and 12% for k_{qm}.

Fig. 1 shows an example of the experimental run for the 0.201 mol/dm^3 PFPE-2-Na solution at 333 K together with the best fitting curve, and the dependence of the A_2, A_3 and A_4 parameters of Eq. (1) is illustrated in Fig. 2 for the 0.39 M PFPE-2-NH$_4$ system at 333 K. Fitting data for the examined samples at various temperatures and quencher concentrations are provided in Supporting Information. In all systems at 303 K and above the A_2 value increases linearly with the MV concentration, the slope of the straight line increasing with temperature, indicating migration of the quencher between micelles. According to the model, the A_3 parameter also increases linearly, while A_4 remains constant within the experimental error. By the iterative treatment of concentration dependencies like those in Fig. 2 we have determined aggregation numbers and kinetic parameters with the uncertainties not higher than 5%, 10% and 16% for N, k_{qm}, and k^-, respectively.

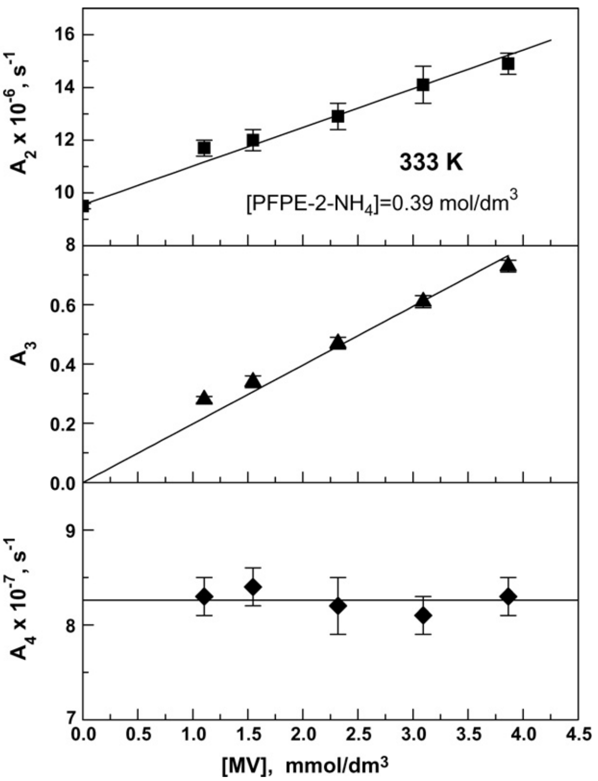

Fig. 2. Dependence of the best fitting parameters of Eq. (1) on the quencher concentration for the 0.390 mol/dm^3 PFPE-2-NH$_4$ solution at 333 K. Each point represents the average value obtained for multiple runs (at least four). The average value of A_4 is $(8.3 \pm 0.1) \times 10^7\ s^{-1}$.

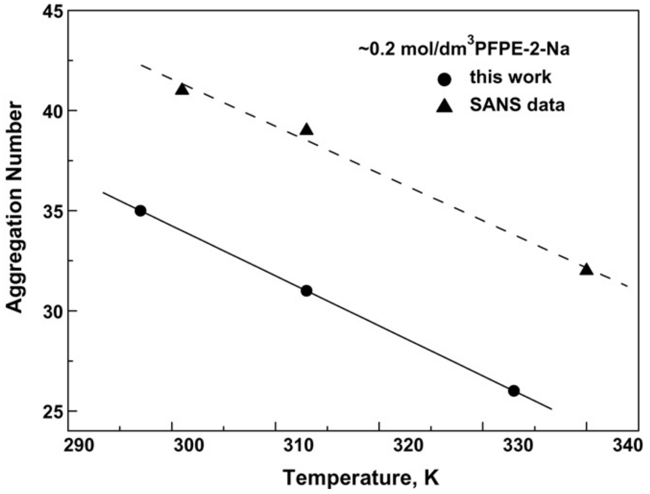

Fig. 3. Temperature effect on the aggregation number in ~0.2 mol/dm^3 PFPE-2-Na solution: (●) TRFQ data and (▲) SANS data, Ref. [8].

In Fig. 3 our N values for the PFPE-2-Na system are compared with those obtained from the SANS study [8]. SANS data are higher by 8 units, and the discrepancy cannot be accounted for by somewhat larger surfactant concentration (0.216 mol/dm^3 as compared to 0.201 mol/dm^3 in our experiments); cf. concentration dependence of N at room temperature reported earlier [5]. In both cases a linear decrease of the aggregation number with increasing temperature is observed, and the slopes of the straight lines are the same within the experimental error.

Similar linear dependencies of N versus temperature are obtained for PFPE-2-NH$_4$ solutions. As seen from Fig. 4, including also SANS data for the surfactant concentration of 0.218 mol/dm^3 [7], the temperature effect on the aggregation number is larger for bigger micelles. While for spherical micelles in the diluted system N decreases only slightly, ellipsoidal micelles in more concentrated systems become considerably smaller. It is relevant to add here that the linear decrease of N with increasing temperature was also reported for other micellar systems [16–18].

According to SANS analysis, assuming close-packed surfactant chains in the hydrophobic core, the aspect ratio of the aggregates formed at room temperature in ~0.2 mol/dm^3 solutions is 2.0 and 2.4 for PFPE-2-Na and PFPE-2-NH$_4$, respectively, but spherical micelle shape was deduced for the sodium salt at 340 K and for the ammonium salt at 353 K [7,8]. Our data suggest that in the case of the 0.39 M PFPE-2-NH$_4$

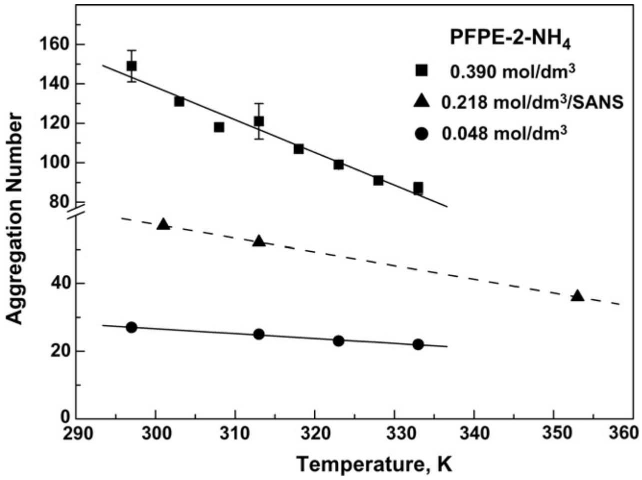

Fig. 4. Temperature effect on the aggregation number in PFPE-2-NH_4 solutions of indicated concentrations: (●, ■) TRFQ data and (▲) SANS data, Ref. [7]. Data for the 0.390 mol/dm^3 system at 297, 313, 323 and 333 K are average values from two experimental sessions for different samples, and error bars represent standard deviations.

solution the large ellipsoids do not transform into spheres in the examined temperature range; the aggregation number at 333 K is 87, while SANS values reported for spherical micelles (in less concentrated systems) are not higher than 40.

Fig. 5 shows Arrhenius plots for the rate constants k^- and k_{qm} in the PFPE-2-NH_4 systems. At a given temperature the rate constant of the quencher exit from micelles is higher in the more concentrated surfactant solution. This finding can be nicely rationalized by the increase of counterion binding to micelles leading to a lower charge density at the interface at higher surfactant concentrations, as indicated in the previous studies [5,7,14]. Weaker electrostatic interactions between the quencher and the micelle result in a higher k^- value (lower probability that the released MV cation becomes re-bound by another charged head group in the vicinity). On the other hand, the activation energy of the quencher exit from ellipsoidal aggregates (390 mmol/dm^3 PFPE-2-NH_4) is significantly larger than the value estimated for spherical aggregates (48 mmol/dm^3 PFPE-2-NH_4), 42 ± 5 kJ/mol as compared to 28 ± 3 kJ/mol. If the exit process was determined only by electrostatic interactions between the quencher cation and the surfactant head-group, one would rather expect a lower activation energy in the former system. Our results imply that hydrophobic interactions also play a role in the binding of the protiated quencher to perfluorinated micelles; these interactions are stronger in larger (ellipsoidal) aggregates.

The 0.201 M PFPE-2-Na solution was examined in less details, yet the activation energy can be roughly estimated from the two k^- data (1×10^6 and $3 \times 10^6\ s^{-1}$ at 313 and 333 K, respectively, while no quencher exit observed at 297 K). The obtained value, ∼50 kJ/mol, is twice as large as that for the 0.48 M PFPE-2-NH_4 solution. Taking into account that both systems comprise micelles of similar aggregation numbers (cf. Figs. 3 and 4), we infer that electrostatic interactions, rather than hydrophobic interactions, are stronger in the case of PFPE-2-Na. Indeed, previous studies suggested higher charge density at the micellar surface in the presence of sodium counterions [5,7,8].

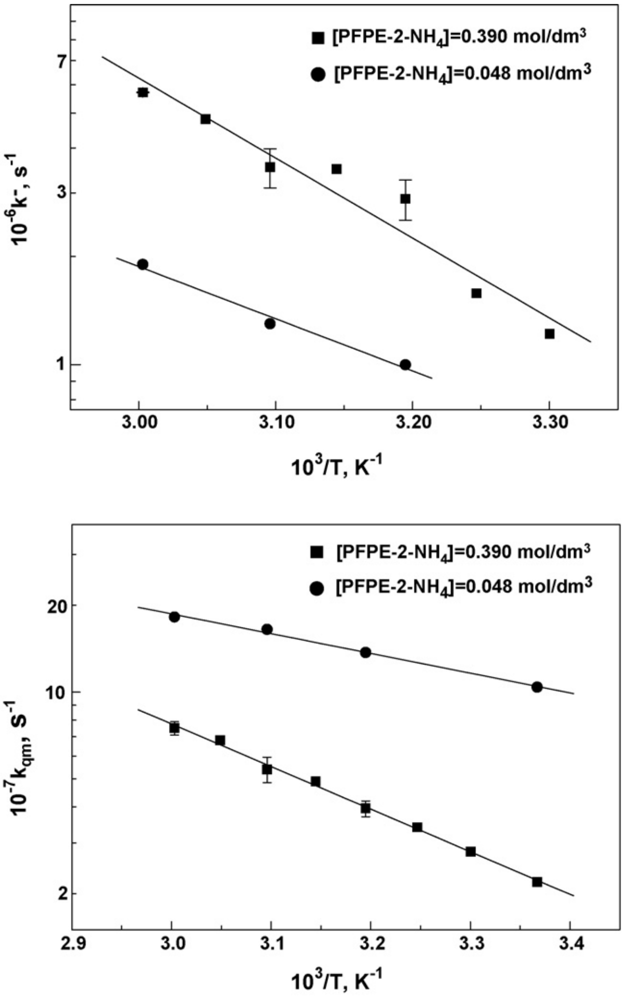

Fig. 5. Arrhenius plots of rate constants of the quencher exit from micelles (k^-, upper panel) and of intramicellar fluorescence quenching (k_{qm}, lower panel) for PFPE-2-NH_4 solutions of indicated concentrations. Data for the 0.390 mol/dm^3 system at 297, 313, 323 and 333 K are average values from two experimental sessions for different samples, and error bars represent standard deviations.

Rate constants of the intramicellar fluorescence quenching in the PFPE-2-NH_4 system are larger for the less concentrated solution (cf. Fig. 5), reflecting higher probability of diffusional encounters of the luminophore and quencher in smaller micelles. Activation energies of this process are 13 ± 1 and 28.2 ± 0.7 kJ/mol for surfactant concentrations 0.048 and 0.390 mol/dm^3, respectively, in comparison to the value 11.7 ± 0.8 kJ/mol obtained for the homogeneous H_2O/PBTMA/MV system. To account for temperature effect on the encounter distance, due to decreasing size of micelles, we have analyzed Arrhenius plots of the product Nk_{qm}, cf. Fig. 6. The activation energies obtained from the Nk_{qm} product correspond to the energetic barrier due to local viscosity [16]. The value estimated for ellipsoidal micelles, 15.9 ± 0.8 kJ/mol, is higher than that for spherical micelles, 8 ± 1 kJ/mol, indicating tighter packing of surfactant molecules in the former system.

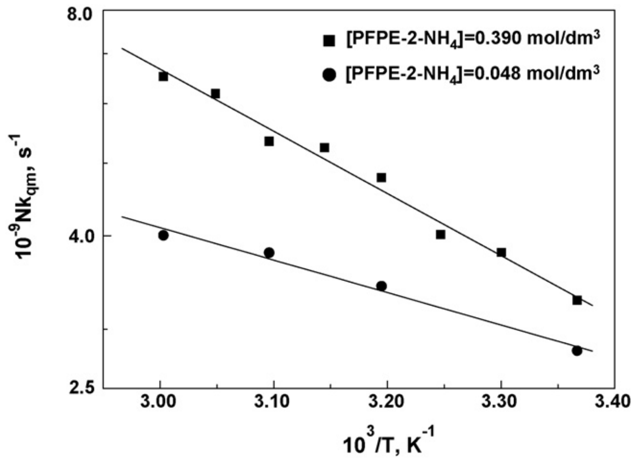

Fig. 6. Arrhenius plots of the product of the aggregation number and the rate constant of intramicellar fluorescence quenching for PFPE-2-NH$_4$ solutions of indicated concentrations.

The results of ESR spin probe studies [15] lead to the similar conclusion.

For the PFPE-2-Na system the activation energy obtained from k_{qm} data (10.2, 12.6 and 13.1 × 10^7 s^{-1} at 297, 313 and 333 K, respectively) is 6 ± 2 kJ/mol. In this system the product Nk_{qm} does not follow the Arrhenius dependence in the whole temperature range, suggesting that ellipsoidal aggregates likely change into spheres already at 333 K. However, the data for 297 and 313 K suggest that the activation energy, corrected for the change in micelle size, equals ~4 kJ/mol; the value is significantly lower than that for spherical PFPE-2-NH$_4$ micelles. This result is also consistent with the ESR studies [15]. The molecular packing in the Na-micelles is less than that in the NH$_4$-micelles.

5. Conclusions

Using PBTMA/MV as a luminophore/quencher pair it is possible to determine aggregation numbers of anionic fluorinated-surfactant micelles by the TRFQ method in a wide temperature range, at least up to 333 K, although above room temperature MV behaves as a mobile quencher and analysis of the kinetic runs is more complex. *N* values obtained for aqueous solutions of PFPE-2-X (X = Na$^+$ or NH$_4$$^+$) surfactants are in a reasonable agreement with those reported from SANS studies; both methods reveal a linear decrease of *N* with increasing temperature. Rate constants of intramicellar fluorescence quenching, and the respective activation energies, indicate the effect of surfactant concentration and of the kind of counterion on molecular packing in the aggregates. The kinetic data for the quencher exit from micelles suggest that binding of the (protiated) probes to large ellipsoidal micelles, formed at high surfactant concentrations, is determined not only by their positive electrostatic interactions with surfactant head-groups, but hydrophobic interactions with fluorinated chains are also important.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2007.03.025.

References

[1] (a) K. Kalyanasundaram, in: V. Ramamurthy (Ed.), Photochemistry in Organized and Constrained Media, VCH Publishers, New York, 1991 (Chapter 2);
(b) C. Bohne, R.W. Redmond, J.C. Scaiano, in: V. Ramamurthy (Ed.), Photochemistry in Organized and Constrained Media, VCH Publishers, New York, 1991 (Chapter 3).
[2] E. Szajdzinska-Pietek, M. Wolszczak, Langmuir 16 (2000) 1675–1680.
[3] P.P. Infelta, M. Grätzel, J.K. Thomas, J. Phys. Chem. 78 (1974) 190–195.
[4] M. Tachiya, Chem. Phys. Lett. 33 (1975) 289–292.
[5] K. Sulak, M. Wolszczak, A. Chittofrati, E. Szajdzinska-Pietek, J. Phys. Chem. B 109 (2005) 799–803.
[6] C.M.C. Gambi, R. Giordano, A. Chittofrati, P. Pieri, P. Baglioni, J. Texeira, Appl. Phys. A 74 (2002) S436–S438.
[7] C.M.C. Gambi, R. Giordano, A. Chittofrati, P. Pieri, P. Baglioni, J. Texeira, J. Phys. Chem. A 107 (2003) 11558–11564.
[8] C.M.C. Gambi, R. Giordano, A. Chittofrati, P. Pieri, P. Baglioni, J. Texeira, J. Phys. Chem. B 109 (2005) 8592–8598.
[9] K. Sulak, J. Winer, M. Wolszczak, A. Chittofrati, E. Szajdzinska-Pietek, in: K.A. Wilk (Ed.), Scientific Conference. Surfactants and Dispersed Systems in Theory and Practice, SURUZ 2005, Korporacja Biznesowa & EDU-SA Wrocław, 2005, pp. 111–114.
[10] C. Tonelli, A. Di Meo, S. Fontana, A. Russo, J. Fluorine Chem. 118 (2002) 107–121.
[11] E. Szajdzinska-Pietek, M. Wolszczak, Chem. Phys. Lett. 270 (1997) 527–532.
[12] R. Roelants, E. Gelade, J. Smid, F.C. De Schryver, J. Colloid Interf. Sci. 107 (1985) 337–344.
[13] A. Chittofrati, R. Pieri, F. D’Aprile, D. Lenti, P. Maccone, M. Visca, Prog. Colloid Polym. Sci. 123 (2004) 23–27.
[14] N. Kallay, V. Tomisic, V. Hrust, R. Pieri, A. Chittofrati, Colloids Surf. A 222 (2003) 95–101.
[15] E. Szajdzinska-Pietek, K. Sulak, I. Dragutan, S. Schlick, J. Colloid Interf. Sci., in press.
[16] H. von Berlepsch, K. Stahler, R. Zana, Langmuir 12 (1996) 5033–5041, and references therein.
[17] H. Huang, R.E. Verrall, B. Skalski, Langmuir 13 (1997) 4821–4828.
[18] S.S. Shah, N.U. Jamroz, Q.M. Sharif, Colloids Surf. A 178 (2001) 199–206.