

# The binding of free calcium ions in aqueous solution using fluoroalkyl end-capped acryloylmorpholine oligomers

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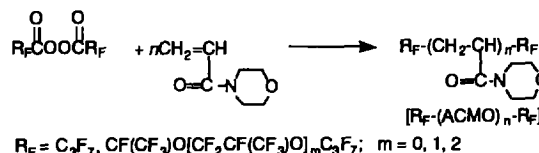
## Abstract

Fluoroalkyl end-capped acryloylmorpholine oligomers which are obtained by the reactions of fluoroalkanoyl peroxides with acryloylmorpholine were shown to have an extraordinarily high calcium binding ability compared with the corresponding non-fluorinated oligomer or the common organic chelating materials such as poly(acrylic acid). © 1997 Elsevier Science S.A.

**Keywords:** Chelating surfactant; Calcium ions; Fluoroalkylated; Acryloylmorpholine; Oligomers

## 1. Introduction

Recently, there has been a great interest in the synthesis and applications of chelating surfactants possessing the functionality of a strong chelate and a surfactant into a single molecule; for example, lauroyl ethylenediaminetriacetate [ $\text{CH}_3(\text{CH}_2)_{10}\text{C}(=\text{O})\text{N}(\text{CH}_2\text{COO}^-)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2^-)_2$ ] was prepared and was shown to combine the properties of strong surfactance and an ability to chelate free ions such as  $\text{Ca}^{2+}$  [1]. In our continuing effort to design and develop new fluoroalkylated functional materials, we have already demonstrated that fluoroalkyl end-capped oligomers, which are prepared by using fluoroalkanoyl peroxides, possess unique properties imparted by fluorine [2]. In particular, fluoroalkylated acrylic acid oligomers [ $\text{R}_F-(\text{CH}_2\text{CHCO}_2\text{H})_n-\text{R}_F$ ;  $\text{R}_F$  = perfluoroalkyl, perfluoro-oxaalkyl groups] were shown to cause an extreme decrease in the surface tension of water to ca.  $15 \text{ mN m}^{-1}$  [3,4], which is almost the same level as that achieved by the usual low molecular weight fluorinated surfactants, and to exhibit biological activities such as anti HIV-1 (human immunodeficiency virus type-1) which cannot be achieved by the corresponding non-fluorinated oligomers [5]. Therefore, it is of considerable interest to apply these fluoroalkylated oligomers as novel fluorinated chelating surfactants. Very recently, we reported that fluoroalkyl end-capped acryloylmorpholine oligomers



Scheme 1.

are obtained by the reactions of fluoroalkanoyl peroxides with acryloylmorpholine, and these oligomers were shown to reduce the surface tension of water quite effectively [6]. Of additional interest, these fluoroalkylated oligomers were also suggested to form intra- or inter-molecular aggregates in aqueous solutions. This result strongly suggests that these oligomers could act as a host molecule for free ions such as calcium ion. Now, we have demonstrated a surprising finding, that fluoroalkyl end-capped acryloylmorpholine oligomers have an extraordinarily high calcium binding ability compared with the corresponding non-fluorinated oligomer or the traditional organic chelating agents such as poly(acrylic acid).

A series of fluoroalkyl end-capped acryloylmorpholine oligomers were prepared according to our previously reported method (as shown in Scheme 1) [6], and the infrared spectra of these oligomers showed the characteristic carbonyl band around  $1640 \text{ cm}^{-1}$ .

The equilibrium calcium ion concentrations in the presence of  $\text{R}_F-(\text{ACMO})_n-\text{R}_F$  [concentration of each oligomer is  $0.5 \text{ g dm}^{-3}$ ;  $\text{R}_F = \text{C}_3\text{F}_7$  ( $0.29 \text{ mmol dm}^{-3}$ ),  $\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$

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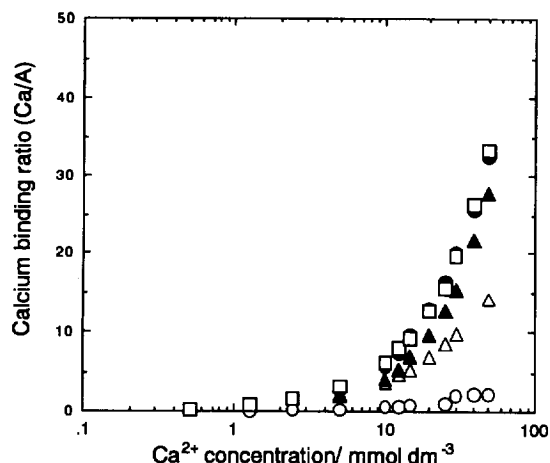


Fig. 1.  $\text{Ca}^{2+}$  binding isotherms of  $\text{R}_F\text{-(ACMO)}_n\text{-R}_F$  ( $0.5 \text{ g dm}^{-3}$ ):  $\square$ ,  $\text{R}_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ ,  $M_n = 7290$ ;  $\bullet$ ,  $\text{R}_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ ,  $M_n = 4730$ ;  $\blacktriangle$ ,  $\text{R}_F = \text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ ,  $M_n = 1860$ ;  $\triangle$ ,  $\text{R}_F = \text{C}_3\text{F}_7$ ,  $M_n = 1700$ ;  $\circ$ ,  $\text{-(ACMO)}_n\text{-}$ ,  $M_n = 3750$ .

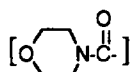
( $0.27 \text{ mmol dm}^{-3}$ ),  $\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$  ( $0.11 \text{ mmol dm}^{-3}$ ),  $\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$  ( $0.07 \text{ mmol dm}^{-3}$ )] were measured by using a calcium ion electrode and a digital pH/ion meter (HORIBA F-23). The results are shown in Fig. 1.

As shown in Fig. 1, it was found that a series of  $\text{R}_F\text{-(ACMO)}_n\text{-R}_F$  have an extraordinarily high calcium ion binding power compared with the corresponding non-fluorinated acryloylmorpholine oligomer [ $\text{-(ACMO)}_n\text{-}$ ]. Calcium binding ratio (Ca/A) indicates the average number of bound calcium ions per two morpholino segments in each oligomer. Especially, longer perfluoro-oxaalkyl end-capped oligomers were shown to have higher Ca/A values than perfluoropropylated one. For example, Ca/As of  $\text{R}_F\text{-(ACMO)}_n\text{-R}_F$  [ $\text{R}_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ ,  $\text{C}_3\text{F}_7$ ] were at maximum 33 and 14, respectively. On the other hand, the corresponding non-fluorinated oligomer:  $\text{-(ACMO)}_n\text{-}$  was hardly effective in removing free calcium ions from solutions. In addition, Ca/A values of fluoroalkylated acrylic acid oligomer [ $\text{R}_F\text{-(CH}_2\text{CHCO}_2\text{H)}_n\text{-R}_F$ ;  $\text{R}_F = \text{CF}(\text{CF}_3)\text{-OC}_3\text{F}_7$ ,  $M_n = 6700$ ] and poly(acrylic acid) were similar to the theoretical binding ratio under the above mentioned analytical conditions. Poly(acrylic acid) is effective in removing calcium ions from solution, however, the binding ratio of poly(acrylic acid) is almost the same as the theoretical binding ratio [7].

There is an obvious correlation between the Ca/A values quoted in Fig. 1 and the reduction of surface tension of water, and as the oligomers have a higher Ca/A value, the oligomers can reduce the surface tension of water more effectively. For example, the surface tensions of water for  $0.5 \text{ g dm}^{-3}$  solutions of  $\text{R}_F\text{-(ACMO)}_n\text{-R}_F$  at  $30^\circ\text{C}$  are as follows [6]:  $19.7 \text{ mN m}^{-1}$  [ $\text{R}_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ ],  $19.9 \text{ mN m}^{-1}$  [ $\text{R}_F = \text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ ],  $33.4 \text{ mN m}^{-1}$  [ $\text{R}_F = \text{C}_3\text{F}_7$ ], and  $63.2 \text{ mN m}^{-1}$  [ $\text{-(ACMO)}_n\text{-}$ ]. Hitherto, hydrophobically modified polyelectrolytes (polysoaps) are well known to exhibit no critical micelle concen-

tration (CMC) or a break point resembling a CMC [8]. In fact, non-fluorinated acryloylmorpholine oligomer was shown to exhibit no CMC or a break point in solutions [6]. However, a clear break point to form intra- or inter-molecular aggregations in aqueous solutions was observed in each fluoroalkyl end-capped acryloylmorpholine oligomer; e.g.  $\text{R}_F\text{-(ACMO)}_n\text{-R}_F$  ( $\text{R}_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ ,  $\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$ ,  $\text{CF}(\text{CF}_3)\text{-OC}_3\text{F}_7$ ) exhibited clear break points at ca.  $0.1\text{--}0.2 \text{ g dm}^{-3}$  [6].

Fluoroalkyl segments in these oligomers are solvophobic in aqueous solutions, and enhance the aggregation due to the strong interaction between fluoroalkyl segments. Very recently, we have found that fluoroalkyl end-capped betaine oligomers [ $\text{R}_F\text{-(CH}_2\text{CHC(=O)NH}_2^+\text{CMe}_2\text{CH}_2\text{SO}_3^-)_n\text{-R}_F$ ] can cause gelation in water owing to the synergistical interaction of the aggregation of fluoroalkyl units and the ionic interactions of the betaine segments under non-cross-linked conditions [9]. Therefore, such interactions of fluoroalkyl units could provide strong aggregation in aqueous solutions, and calcium ions should act as guest molecules for these aggregates. *N*-Morpholinecarbonyl segments



would act as suitable host moieties in these aggregates, and interact strongly with calcium ions.

Hitherto, it is well known that organic chelating materials such as 1,3-diketones, phosphates, poly-electrolytes such as poly(acrylic acid), poly(maleic acid) and water soluble polymers with 8-quinolinol groups, EDTA (ethylenediaminetetraacetic acid) and its derivatives are effective in removing free metal ions from solution [1,7,10]. However, to our knowledge, this is the first example which shows that *N*-morpholinecarbonyl segments are applicable as chelating agents. Further extension to the synthesis and properties of various fluoroalkyl end-capped acryloylmorpholine derivatives are now being studied.

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