Colloid Polym Sci 273:520–523 (1995)

ORIGINAL CONTRIBUTION

A. A. Klyamkin
I. N. Topchieva
V. P. Zubov

Monomolecular films of pluronic-cyclodextrin inclusion complexes at the water-gas interface

Received: 31 January 1994
Accepted: 17 August 1994

A. A. Klyamkin · I. N. Topchieva
V. P. Zubov
Polymer Science Department,
Faculty of Chemistry
Moscow State University
Moscow Russia, Shemyakin Institute
of Bioorganic Chemistry
Russian Academy of Science, Moscow
Russia

Abstract This paper reports the synthesis and characteristics of inclusion type complexes between amphiphilic block copolymer of ethylene and propylene oxides (pluronic) and α–, β–, and heptakis-(2,6-di-O-methyl)-β–cyclodextrins. The process was investigated in monolayers at the water-gas interface according to Langmuir-Blodgett technique. Pluronic forms a monolayer, stable at the surface pressure 5 mN/m, which reacts with heptakis-(2,6-di-O-methyl)-β–cyclodextrin and does not react with α– and β–cyclodextrins. The absence of the reaction in the case of α–cyclodextrin is explained by the fact that the polymer guest does not fit into a small cavity of the macrocyclic host, but for β–cyclodextrin it may be explained by its low surface activity and, hence, its low local concentration in the vicinity of the pluronic monolayer. After introducing heptakis-(2,6-di-O-methyl)-β–cyclodextrin into the aqueous subphase under the pluronic monolayer an instant increase in the area is observed. An increase in the amount of heptakis-(2,6-di-O-methyl)-β–cyclodextrin in the aqueous phase causes first steep linear increase in the monolayer area, then its leveling off at the polymer - heptakis-(2,6-di-O-methyl)-β–cyclodextrin ratio equal to about 1:15. This value correlates well with a stoichiometric composition of the similar complex in solution.

Key words Monolayer – pluronic – cyclodextrin – Langmuir-Blodgett technique

Introduction

Of much significance is an interaction between macromolecules and small molecules (ligands) in many areas including living systems. Molecular recognition on biomembrane surfaces is an important example of such a specific intermolecular interaction. Organized monolayers can be considered as models of biomembranes providing a convenient system for studying molecular interactions and, consequently, for molecular recognition [1]. In this respect it was interesting to study molecular interactions between synthetic polymers and cyclic oligosaccharides-cyclodextrins (CD) at the water-air interface using the Langmuir-Blodgett (L-B) technique.

The tendency of CD to form inclusion complexes with hydrophobic compounds of various chemical nature is well documented [2]. The study of the interaction of CD with macromolecular compounds is in an early stage. One of the latest reports by Harada and Kamachi describes complexes with polyoxypropylene and polyoxyethylene oligomers [3–5]. They treat these complexes as an essential new type of inclusion compound in which a single host polymer molecule is immobilized by several CD molecules. Using amphiphilic block copolymers of ethylene oxide and propylene oxide (pluronics) in which poly(ethylene oxide)

is a hydrophilic block and poly(propylene oxide) is a hydrophobic block (instead of using homopoly(alkylene oxide)) makes possible to design complexes with diverse molecular architecture and properties.

It was established earlier that in an aqueous phase pluronics form complexes with β– and dimethyl-β–CD and do not form complexes with α–CD (for steric reasons) [2]. It comprises a polymer chain performing as a guest molecule and a sequence of CD threaded onto a polypropylene oxide (PPO) block. The packing of this fragment may involve intermolecular contacts via hydrogen bonding between the ethylene oxide (PEO) block and primary hydroxyl groups of CD. Here, the stoichiometry corresponds to one CD molecule per two propylene oxide monomeric units (for pluronic L-61 used in this investigation it was 18 CD molecules per one polymer molecule) [6].

This paper reports the synthesis and characteristics of inclusion type complexes between amphiphilic block copolymer of ethylene and propylene oxides (pluronic) and α–, β–, and dimethyl-β–CD. The process was investigated in monolayers at the water-gas interface according to L-B technique.

Experimental

A block copolymer of ethylene oxide and propylene oxide, pluronic L-61 (M_n = 2000) from Serva (FRG)

$$HO\text{–}(CH_2\text{–}CH_2\text{–}O)_3\text{–}(CH_2\text{–}\underset{\displaystyle CH_3}{\underset{|}{C}}H\text{–}O)_{30}\text{–}(CH_2\text{–}CH_2\text{–}O)_3\text{–}H,$$

was used without preliminary purification.

α–Cyclodextrin (α–CD), β–Cyclodextrin (β–CD), and heptakis-(2,6-di-O-methyl)-β–cyclodextrin (methyl-CD) were purchased from Chinoin (Hungary) and used without preliminary purification.

All the experiments on monolayers were performed on Langmuir balance, Lauda FW2 (FRG) (volume of the bath is 1.5l), at 293 K.

The isotherm of the surface pressure (p) versus area per molecule (S) for all compounds is measured at 293 K with a compression rate 50 sm^2/min. Error in the experiment was less then 2%. All curves were reproduced three times or more.

Two mkl of pluronic dissolving in chloroform ($C = 3.6 \cdot 10^{-3}$ M) was introduced at the water-air interface. After chloroform evaporation the monolayer is compressed up to 5 mN/m surface pressure and kept under this pressure for 1 h. Then, cyclodextrin in necessary amounts (V = 0.5 – 400 mkl; $C = 10^{-2}$ M) was introduced in the aqueous subphase, and change in the area was registered.

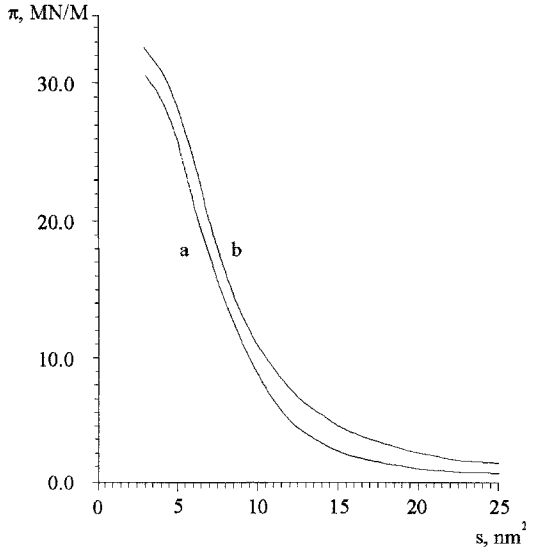
Results and discussion

Surfactant properties of pluronic and cyclodextrins were preliminary evaluated. It was found that methyl-CD and pluronic form, but α–CD and β–CD do not form monomolecular films at the water-air interface under these conditions. The dependence of surface pressure (p) versus area per molecule (S) of pluronic and methyl-CD are shown in Figs. 1a and 2. According to Fig. 1a, pluronic forms a stable monolayer existing in liquid-expanded and liquid condensed states (the border is around 10 mN/m), methyl-CD forms an unstable monolayer which exists only in a liquid expanded state.

After introducing α–CD in the aqueous subphase practically no change in the value of area of the pluronic monolayer is observed. This apparently is assigned to the absence of the reaction between α–CD and poly(propylene oxide) that occurs because the polymer guest does not fit into a small cavity of the host [5]. The absence of interaction of the two components in monolayer evidently correlates with their behavior in solution.

When β–CD was added to the aqueous phase the area of the pluronic monolayer changed insufficiently (≈ 3–5% from initial area), probably because pluronic and β–CD did not interact in the monolayer, despite that these compounds form a complex in solution. This phenomenon may be explained by the low surface activity of the β–CD.

Fig. 1 Surface pressure-area per molecule isotherms for pluronic L-61 (a) and the complex of L-61 with methyl-CD (b). T = 293 K



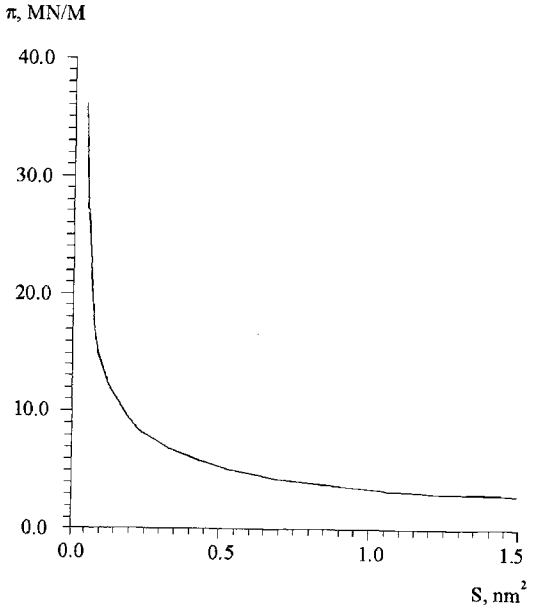


Fig. 2 Surface pressure-area per molecule isotherms for CH_3-CD. $T = 293$ K

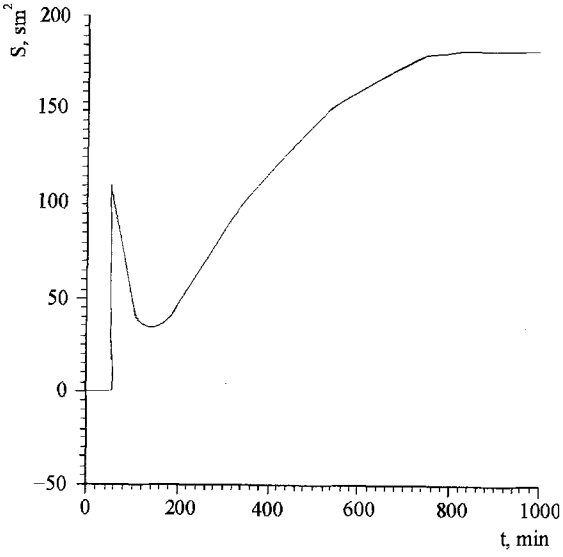


Fig. 3 Curve of monolayer area versus time of interaction between pluronic and methyl- CD, $p = 5$mN/m, $T = 293$ K

Due to this fact local concentration of β–CD in the vicinity of the pluronic monolayer does not exceed its average concentration in the aqueous subphase. At the pluronic: β–CD ratio 1:1000 – the concentration of β–CD is 10^{-6} M and the interaction between the two substances proceeds at a very low rate.

After introducing methyl-CD into the aqueous subphase under the pluronic monolayer, an instant increase in the area value on the area-time curve is observed in every case (Fig. 3). Perhaps, this occurs due to the distortion of the pluronic monolayer as a result of a quick insertion of the surface active methyl-CD into the subphase. A monotonous increase in the monolayer area up to its maximum value is then observed for 10–12 h (Fig. 3). The monolayer is expanded up to 35% as compared to its initial area, apparently because of the formation of the complex between pluronic and methyl-CD at the water-gas interface, similarly to their interaction in solution [7].

This is supported by data of monolayer area versus amount of methyl-CD added to the aqueous phase curve (Fig. 4). As seen in Fig. 4, an increase in the amount of methyl-CD in the aqueous phase first causes steep linear increase in the monolayer area, which then levels off at a polymer – methyl-CD ratio of about 1:15. This curve resembles the titration curve, and it is supposed that all molecules of methyl-CD react with pluronic ones; the stoichiometry between them is also equal 1:15. This value correlates well with the stoichiometric composition of a similar complex in solution. [6].

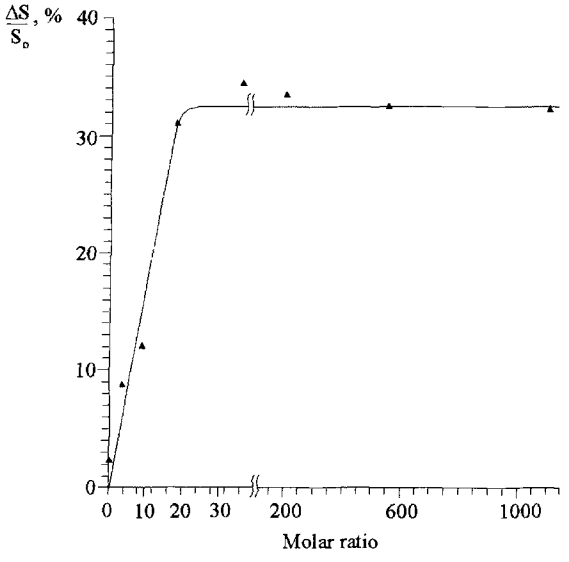


Fig. 4 Plot of monolayer area after reaction versus amount of methyl-CD added to the aqueous phase. $p = 5$mN/m, $T = 293$ K

The linear character of this curve from zero practically up to its break point gives evidence for very high stability of the complex between pluronic and methyl-CD.

Figure 1b shows the plot of the surface pressure versus area per molecule for the monolayer of the pluronic – methyl-CD complex. The comparison of this curve with the p-S curve of the pluronic layer shows that the characters of both plots are very similar. But the area per mole-

cule and collapse pressure for the complex are higher than for the pluronic itself. Modeling of the structure of the complex between methyl-CD and pluronic using Stewart-Breigleb atomic models and data of pulsed ^{1}H-NMR spectrum indicates that this molecule has a rod-like conformation. The conformation should provide more dense packing in the monolayer, which explains an increase in the collapse pressure as compared with the pluronic monolayer.

Thus, the complex formation between pluronic and cyclodextrins, previously discovered in aqueous solution, can proceed in the monolayer. Necessary conditions for this interaction are steric conformity of the host and guest molecules and the surface activity of the two components.

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