Phytotoxic Effects of Dimeric Cationic Surfactant Gemini (16-2-16), (16-6-16) and (16-10-16)

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***Abstract*—**In this study, the gemini surfactants of the alkanediyl-a-x-bis(alkyl dimethyl ammonium) dibromide type, with n-C16 alkyl groups and different spacers containing s carbon atoms, referred to as ''16-s-16'' (s = 2, 6, 10) were selected to examine their phytotoxic effects. These dimeric cationic gemini surfactants were synthesized in our laboratory. They were evaluated under laboratory conditions using onion (Allium cepa L.) as a test material. The phytotoxic effects on root were determined after 7th days. Surfactants used in study were tested at three different surfactant concentrations, 2.00, 1.00 and 0.5 g/L concentrations. The phytotoxicity results were based on the effective concentration that reduced root growth by 50 % (EC50). Some differences were observed between the effects of three types of gemini surfactants. Stimulatory effects only occurred in Gemini (16-2-16) at 0.5 g/L concentration, while inhibitory effects occured in Gemini (16-6-16) and Gemini (16-10-16) at all concentrations and in Gemini (16-2-16) at 2.00 and 1.00 g/L concentration. It was observed that inhibitory effects increased with increasing concentrations of in Gemini (16-6-16) and Gemini (16-10-16).

***Keywords*—**Cationic gemini surfactant, Effect, CG (16-2-16), CG (16-6-16), CG (16-10-16), Onion.

I. Introduction

SURFACTANTS have been widely used in industrial, biological, pharmaceutical, and cosmetic systems [1]. Surfactants made up of two identical single-chain amphiphilic structures connected close to the head groups through a spacer chain are referred to as gemini or dimeric surfactants [2]. These compounds have two hydrophilic groups and two hydrophobic groups per molecule, while conventional single-chain surfactants have one hydrophilic and one hydrophobic group per molecule (Fig.1) [3].

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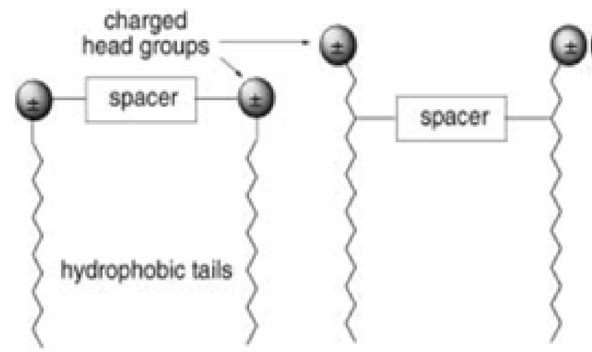


Fig. 1 The basic structure of gemini (twinned) surfactants.

Several reasons can be given for the present interest in gemini surfactants [4]. These gemini compounds appear to be superior to the conventional single-chain surfactant in many properties such as lower critical micelle concentration (CMC) and better wetting, foaming, and dispersing properties [4], [5]. Owing to such superior properties, gemini surfactants have been considered surfactants for the future [3], [6]. They have been used in various areas, such as skin and body care products, food industry [7], oil recovery, gene delivery (CG) drug entrapment and release [8], antimicrobial products [9]. Recently they have also found their way in synthesizing various mesoporous and nanostructured materials [10]. Surfactants are widely used in many fields and exert both beneficial and toxic effects. They bind to proteins as well as to phospholipids influencing (stimulating or inhibiting) enzyme activity and membrane permeability. There are lots of studies about the effects of surfactants on plants. Surfactants make stimulatory effects [11], [12], [14] and also have phytotoxic effects [13], [15], [16], [17]. As recent research indicates, the biological effects strongly depend on the structure of surfactants [12], [14]. Consequently, the effects of surfactants have a marked impact on human health care, biotechnology, environmental protection and agrochemistry. It is important that the determined EC_{50} concentrations are close to control values. In addition, it must be selected an appropriate surfactant which has minimal toxicity and maximal benefits for each purpose. Surfactants have the potential to pose environmental problems unless they are used in a well-controlled manner. Anionic surfactants, used as the main cleaning agents in most laundry detergents, are not generally absorbed by inorganic solids, but cationic surfactants are strongly absorbed by solids, particularly clays. Therefore, it is important to understand phytotoxic effects of these surfactants on several kinds of plants. The aim of this study was to investigate the phytotoxic effects of different cationic gemini (16-2-16, 16-6-16, 16-10-16) surfactant solutions on root growth under laboratory conditions using onion (*Allium cepa*) as a test material.

II. Material And Methods

A. Materials

Cationic surfactants: The cationic gemini surfactants; N,N'dihexadecyl-N,N,N',N-tetramethylN,N-ethanediyl-diammoniumdibromide (16-2-16) N,Ndihexadecyl-N,N,N',N'-tetramethylN,N-hexanediyldiammonium dibromide(16-6-16) N,Ndihexadecyl-,N,N,N'N'-tetramethylN,N-decanediyldiammoniumdibromide16-10-16)

TABLE I
CHARACTERIZATION OF THE EXPERIMENTAL SURFACTANTS

Surfactant symbol	Structral formula
Gemini (16-2-16)	
N,N' dihekzadesil-N,N,N',N'-tetrametil-N,N'-etandiyl-diamonyum dibromür	$C_{16}H_{33}N+(CH_3)_2$-CH_2-(CH_2-$OCH_2)_2$-CH_2-$+(CH_3)_2C_{16}H_{33}$, 2Br-
Gemini (16-6-16)	
N,N'-dihekzadesil-N,N,N',N'-tetrametil-N,N'-hekzandiyl-diamonyum dibromür	$C_{16}H_{33}N+(CH_3)_2$-CH_2-(CH_2-$OCH_2)_6$ -CH_2-$+(CH_3)_2C_{16}H_{33}$, 2Br-
Gemini (16-10-16)	
N,N'-dihekzadesil-N,N,N',N'-tetrametil-N,N'-dekandiyl-diamonyum dibromür	$C_{16}H_{33}N+(CH_3)_2$-CH_2-(CH_2-$OCH_2)_{10}$ -CH_2-$+(CH_3)_2$C16H_{33}, 2Br-

have been synthesized, purified and characterized in our laboratory according to the procedure reported by Zana et al.[18]. The original materials for the synthesis of the cationic geminis, alkanediyl-α-ω-bis (alkyldimethyl ammonium) dibromides: 1-bromohexadecane (97%, Fluka), N,N,N',N'-tetramethyl ethylen ediamine (98 %, Fluka), 1,6-dibromohexane, (97 %, Fluka), 1,10-dibromodecane, (95 %, Fluka), N,N-dimethylhexadecyl amine (98%, Fluka), were used without further purification. Surfactant purity was checked by nuclear magnetic resonance (NMR) and surface tension, all with excellent results. 1H NMR spectra were recorded in CDCl3 solution with a Varian Mercury Plus 300 MHz spectrometer. 13C NMR spectra were recorded at 75 MHz. [19]. Their Characterization were given in Table 1.

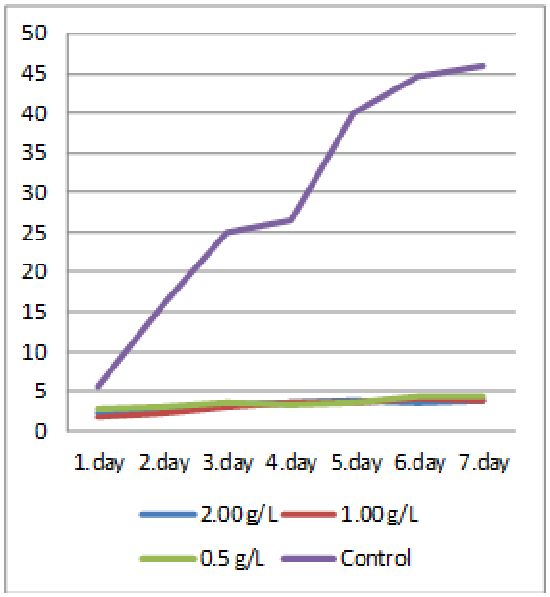
B. Methods

Trade names for these cationic gemini surfactants are CG (16-2-16), (16-6-16) and (16-10-16). They were evaluated under laboratory conditions using onion (*Allium cepa L.*) as a test material.These surfactants were selected because they represent important groups being used in the academic and industrial areas. Onion (*Allium cepa*) was selected as a material for this study. Because it grows rapidly and has got much absorption surface, onion is a good material for this study. *Allium cepa* is currently the third largest fresh vegetable industry in same places. All experiments were performed on primordial root of the onion. Healthy and equal-sized bulbs of common onion were used. Twelve onions composed an experimental set including three of them were control. Onions were placed individually in 60 mL vessels at the beginning of the experiment containing different surfactants. The temperature of the laboratory was kept at 16 ± 0.5 ºC. Surfactants used in study were tested at three different surfactant concentrations, 2.00, 1.00 and 0.5 g/L concentrations. Root lengths were measured using a millimeter ruler starting at the onset of incubation, then after 1st, 2nd, 3rd, 4th, 5th, 6th and 7th days. At the end of the 7th day, the total root lengths were measured. The phytotoxicity results were based on the effective concentration that reduced root growth by 50 % (EC50). The phytotoxic effects on root were determined after 7th days [11-17].

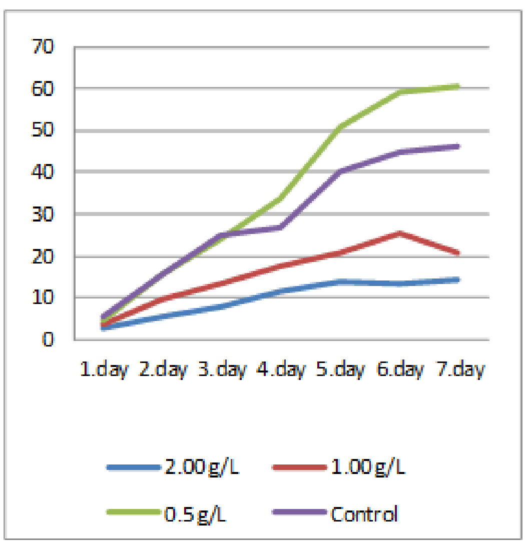
III. Result And Discussion

In this study, the phytotoxic effects were observed on onion roots which were treated by all surfactant solutions described above. Stimulatory effects were observed only on roots of onions treated by Gemini (16-2-16) (Fig.2b). The effects of surfactants on *A. cepa* root elongations after 7-days were varied by surfactant types. As seen as Figs. 2, 3 CG (16-6-16) and CG (16-10-16) was more toxic than CG (16-2-16). The highest phytotoxic effects were observed for CG (16-6-16) and CG (16-10-16) solutions at all doses (Fig.2a.c). When we compared the phytotoxic effect of CG (16-2-16) doses, that of 2.00 g/L was found to be very toxic. EC concentration of CG (16-2-16) was determinated to be 1.00 g/L dose (Fig. 2b). Stimulatory effects were observed only 0.5 g/L. Dose (Fig. 2b). The effects of cationic gemini treatments on *A. cepa* root elongations after 7-days are given (Fig. 3).

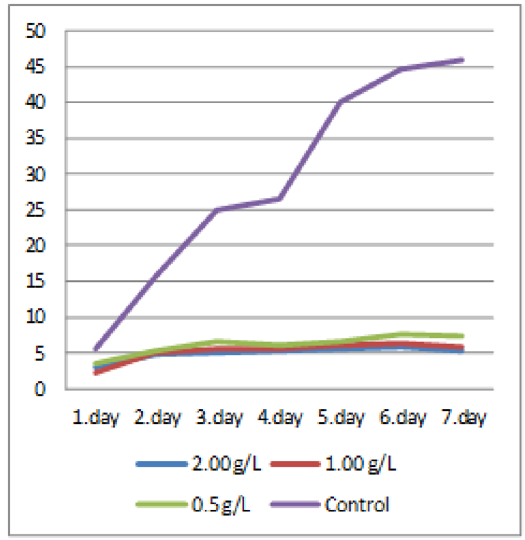
In previous studies CG (16-2-16) as used in this study, concentrations were found to be very toxic at 0.5%, 0.25%, and 0.125% (w/v) levels [11]. In our last study [17] diluted concentrations of CG (16-2-16) were used at three different concentrations (stock solution contains 5 g. sur./1000ml water) (1/8) and diluted solutions of (1/16) and (1/32)) were used (0,05%, 0.02%, 0,01% (w/v) concentrations) and it was seen it had stimulatory effects at all doses. In lower concentrations of CG (16-2-16) were seen stimulatory effects. In our another studies [12], it was found that TX-100 and TX-114 surfactants were very toxic for *Allium cepa*. Stimulatory effect of TX-405 was seen obviously while phytotoxic effects of TX-100 and TX-114 were determined. EC_{50} concentration of TX-100 was found at 1.25 g/L concentration. Also stimulatory effects were seen on the root elongation of onion (*Allium cepa* L.) treated by Brij 35, Brij 56, Brij 76, POE 10. It was found that the stimulatory effects of surfactants was detected in the number of the ethylene oxide groups and the hydrofobic state of surfactant[14]. In this study, a correlation was obtained between the degree of phytotoxicity that toxic effects of CG is related with the different spacers containing s carbon atoms and doses were applied. Physical and chemical characteristics of CG was nearly the same for cationic gemini (16-6-16) and (16-10-16) and (16-2-16). Only the s values were different.



(a) CG16-6-16



(b) CG16-2-16



(c) CG 16-10-16

Fig. 2 The mean of root elongations affected by three cationic gemini surfactant solutions after 7 days

a. CG 16-6-16; b. CG16-2-16; c. CG 16-10-16.

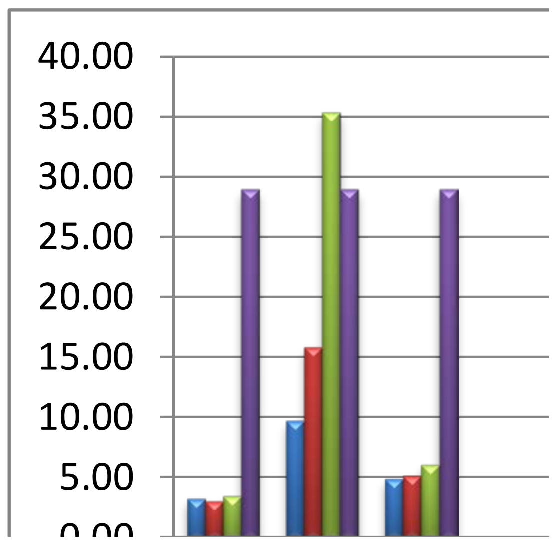


Fig. 3 The means of onion root lengths treated by three cationic gemini surfactants during 7 days.

IV. Conclusion

Consequently, cationic Gemini (16-2-16) (16-6-16) and (16-10-16) have different effects on roots of onion. Gemini (16-6-16) and (16-10-16) is very toxic at all concentration for onion. Gemini (16-2-16) is very toxic at 2.00 g/L concentration and EC50 concentration of was found at 1.00 g/L concentration but it is not toxic at 0.5 g/L concentration and also it has as stimulatory effects at this concentration. The phytotoxic effects of CG is related with the different spacers containing spacers carbon atoms and doses were applied.

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