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ORIGINAL CONTRIBUTION

Extraction of water miscible organic dyes by reverse micelles of alkyl glucosides

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Abstract The extraction of methyl orange or methylene blue from an aqueous phase to an organic phase of reverse micelles of alkyl glucosides was investigated. Dodecyl glucoside, a biodegradable and biocompatible surfactant, was employed as a kind of alkyl glucosides, since a stable Winsor II system consisting of the water-in-oil type microemulsion and aqueous phases was formed when an organic solution containing dodecyl glucoside was contacted with an aqueous solution. The water content in the reverse micellar organic phase increased with an increase in the concentration of dodecyl glucoside. The extraction ratio of dyes also increased with increasing the concentration of dodecyl glucoside. Furthermore, the extraction ratio of dyes was dramatically dependent upon the pH of an aqueous phase and temperature.

Keywords Reverse micelle · Extraction · Organic dye · Nonionic surfactant · Alkyl glucoside

Introduction

Organic dyes, which are contained in effluents of industries such as textiles, pulps, paper making, and paints, are hazardous and adversely affect the ecosystem [1]. Therefore, increased attention has been given to the development of efficient methods for the removal of dyes from waste water. As a traditional method of removing dyes from waste water, oxidation methods such as UV/ozone and UV/H_2O_2, adsorption, and flocculation–precipitation have been studied. However, oxidation methods effectively work only for low concentrations of dyes, it is difficult to regenerate adsorbents after adsorption, and it is impossible to reuse dyes because of the formation of a stable dye–flocculant complex.

In the present work, we have employed liquid–liquid extraction by reverse micelles in order to remove dyes from waste water. Liquid–liquid extraction has ease of separation and offers the advantages of economy of scale observed in the traditional chemical process industries. Reverse micelles are nanometer-sized aggregates of surfactant molecules dispersed in a hydrophobic organic phase like octane, which form thermodynamically stable water-in-oil (w/o) type microemulsions containing a small amount of water in their centers. Since water-soluble substances are entrapped into each water droplet of the microemulsion, reverse micelles have been utilized for the extraction process of proteins as a novel extractant [2–4] and the protein refolding as an artificial chaperone [5]. In order to form reverse micelles, ionic surfactants such as sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and cetyltrimethylammonium bromide have mainly been used. On the other hand, it has been reported that many kinds of surfactants have several types of toxicity to aquatic organisms [6, 7]. In our present study, we used alkyl glucoside as a surfactant, since alkyl glucoside has biodegradability and biocompatibility, and is widely used as a detergent for dishes and shampoo.

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Experimental

Dodecyl glucoside (DG) consisting of monoglucoside (75%), diglucoside (20%), and triglucoside (5%) as a hydrophilic group was supplied from Gun Ei Chemical Industry (Gunma, Japan). The structure of dodecyl monoglucoside, which is the principal constituent of DG, is shown in Fig. 1. The hydrophile–lipophile balance value of DG was 10. The surfactant was used without further purification. Methyl orange and methylene blue were obtained from Kanto Chemicals (Tokyo, Japan). Isooctane and *n*-butanol were from Kanto Chemicals (Tokyo, Japan) and were of analytical grade.

The limiting amount of water solubilized by DG in an organic phase was measured as follows. Isooctane/*n*-butanol (7:3 (*v*/*v*)) containing a certain amount of DG and distilled water were contacted in a 1:1 volume ratio at 25 °C and 120 rpm for 1 h. After the incubation, the organic phase was centrifuged at 4,000 rpm for 30 min. The water concentration of the organic phase after centrifugation was determined by the optimized Karl Fisher potentiometric titration using a Hiranuma AQ-6 aquacounter.

The extraction of methyl orange or methylene blue was mainly performed by contacting isooctane/*n*-butanol (7:3 (*v*/*v*)) containing 50 g/L DG and an aqueous solution containing 50 μM methyl orange or methylene blue in a 1:1 volume ratio at 25 °C and 120 rpm for 2 h. After extraction, the organic phase was centrifuged at 4,000 rpm for 30 min, and the concentration of methyl orange or methylene blue in the organic phase was measured spectrophotometrically by a UV/vis spectrophotometer (Ubest-55, Japan Spectroscopic Co. Ltd.).

The extraction ratio (R) is defined as

$$R = M_{\mathrm{R}}/M_{\mathrm{F}} \tag{1}$$

where M_{F} and M_{R} are number of moles of dyes in an aqueous phase before extraction and number of moles of dyes in an organic phase after extraction, respectively.

Results and discussion

The extraction system with reverse micelles has been carried out on the basis of the formation of a Winsor II system consisting of the w/o type microemulsion and aqueous phases and the solubilization of w/o type microemulsions [2]. A stable Winsor II system was found to be formed when an organic solution containing DG was contacted with an aqueous solution.

In order to examine the solubilization capacity of water by DG, the limiting amount of solubilized water by DG in the organic phase was measured as a function of the concentration of DG at 25 °C. The results are in Fig. 2. The limiting amounts of water increased abruptly at 1.3 g/L DG, followed by a linear increase. Such an abrupt increase in the limiting amounts may be due to the fact that reverse micelles are formed above 1.3 g/L DG in the organic phase. Thus, the apparent critical micelle concentration (cmc) of DG is considered to exist around 1.3 g/L, since the organic phase measured in the range from 0 to 50 g/L DG was transparent. We have reported that in isooctane/*n*-butanol (7:3 (*v*/*v*)), the apparent cmc of DK-F-110, which is a nonionic surfactant and equivalent weight mixture of sucrose monoesters and polyesters of stearic acids, is 10 g/L [2]. The solubilization capacity of water by DG is comparable to that by DK-F-110.

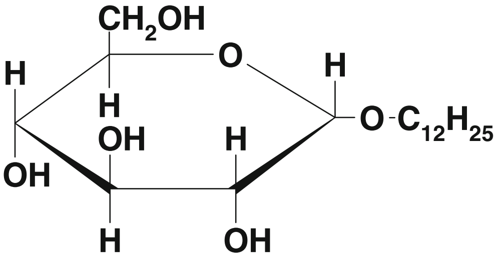

Fig. 1 Structure of dodecyl monoglucoside

We used methyl orange as an anionic dye and methylene blue as a cationic dye in Fig. 3. Comparison of solubilization capacities of methyl orange and methylene blue by DG as a function of time of extraction at pH 7 is shown in Fig. 4. Extraction ratios of these two dyes in the organic phase increased with an increase in time of extraction and reached a plateau around 120 min. The extraction ratio of methyl orange was 0.7 at 120 min while that of methylene blue was 0.1.

In order to examine the solubilization capacity of dyes by DG, the extraction ratios of methyl orange and

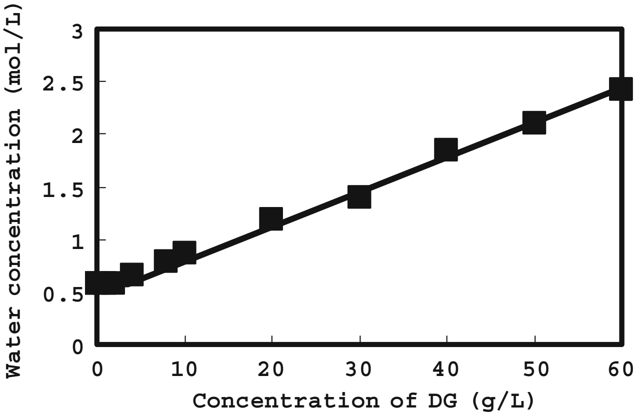

Fig. 2 Dependence of water concentration in the organic phase containing DG on the concentration of DG. The incubation was carried out at 25 °C and 120 rpm for 1 h

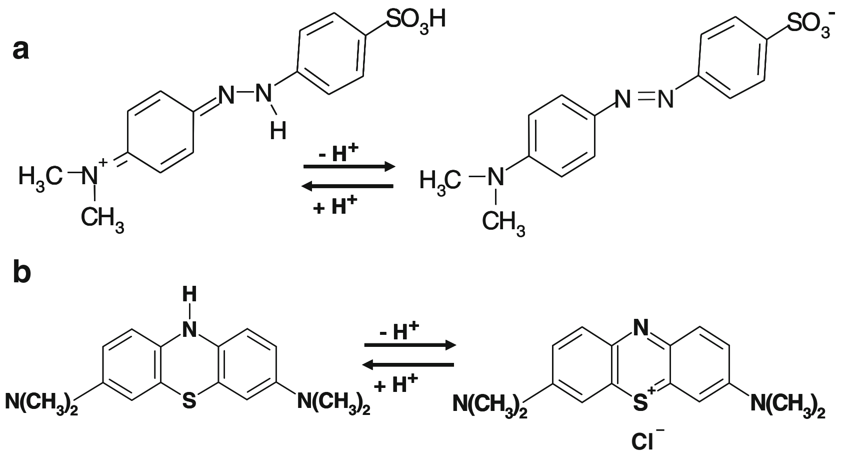

Fig. 3 Structure of dyes: **a** methyl orange, **b** methylene blue

methylene blue were measured as a function of the concentration of DG at pH 7 and 25 °C. As shown in Fig. 5, methyl orange and methylene blue were not transferred from an aqueous phase to an organic phase without DG. The extraction ratio of methyl orange gradually increased till 10 g/L DG and drastically increased above 10 g/L DG. The extraction ratio of methylene blue increased above 10 g/L DG as well, although methylene blue was scarcely extracted in the organic phase till 10 g/L DG.

As mentioned above, the extraction efficiency of methyl orange is much different from that of methylene blue. In order to evaluate the solubilization states of these two dyes in DG reverse micelles, we examined absorption spectra of methyl orange and methylene blue in DG reverse micelles since these two dyes are used as absorption probes to investigate the microenvironment in reverse micelles [8, 9]. Figure 6a shows absorption spectra of methyl orange in water and in DG reverse micelles. The absorption maximum of methyl orange in water was 465 nm while that in DG reverse micelles was 413 nm. It has been reported that the absorption maximum is blue-shifted with decreasing the polarity of solvents [8]. The electronic transition energy of methyl orange molecules, as reflected in the wavelength of their absorption maxima, is an indication of the polarity of their microenvironment. Figure 6b shows absorption spectra of methylene blue in water and in DG reverse micelles. The absorption maxima of methylene blue in water and in DG reverse micelles were 663 and 660 nm, respectively. It has been reported that there are three types of water in the water pool of the reverse micelles of poly(oxyethylene) nonylphenyl ethers in cyclohexane: (1) water interacting directly with the oxyethylene groups of the surfactant, (2) bound water next to the hydrated oxyethylene groups, and (3) bulk like water [10]. Three types of water are respectively referred as primary bound water, secondary bound water, and free water. The polarities of primary and

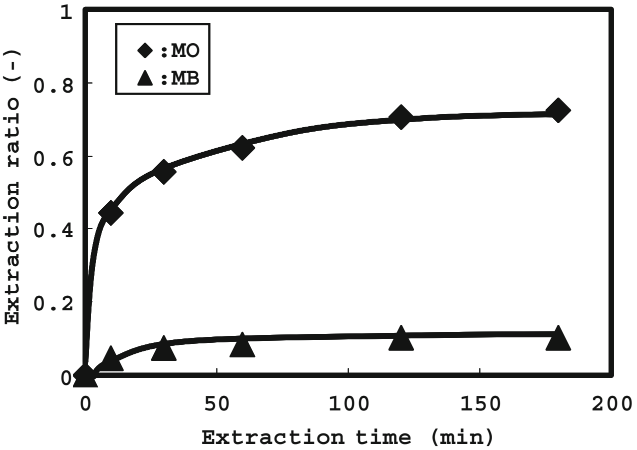

Fig. 4 Time course of extraction ratios of methyl orange and methylene blue at pH 7. Isooctane/*n*-butanol (7:3 (*v*/*v*)) containing 50 g/L DG was used as an organic phase, while a buffer solution of 0.01 M containing 50 μM methyl orange (*MO*) or methylene blue (*MB*) was used as an aqueous solution. The extraction was carried out at 25 °C and 120 rpm

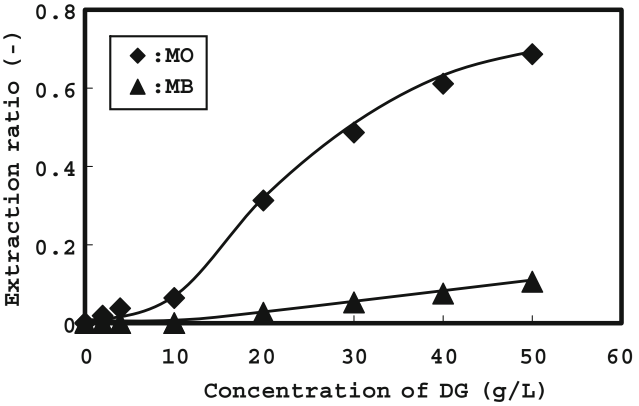

Fig. 5 Dependence of extraction ratios of dyes on the concentration of DG at pH 7. Isooctane/*n*-butanol (7:3 (*v*/*v*)) containing a certain amount of DG was used as an organic phase, while a buffer solution of 0.01 M containing 50 μM methyl orange (*MO*) or methylene blue (*MB*) was used as an aqueous phase. The extraction was carried out at 25 °C and 120 rpm for 2 h

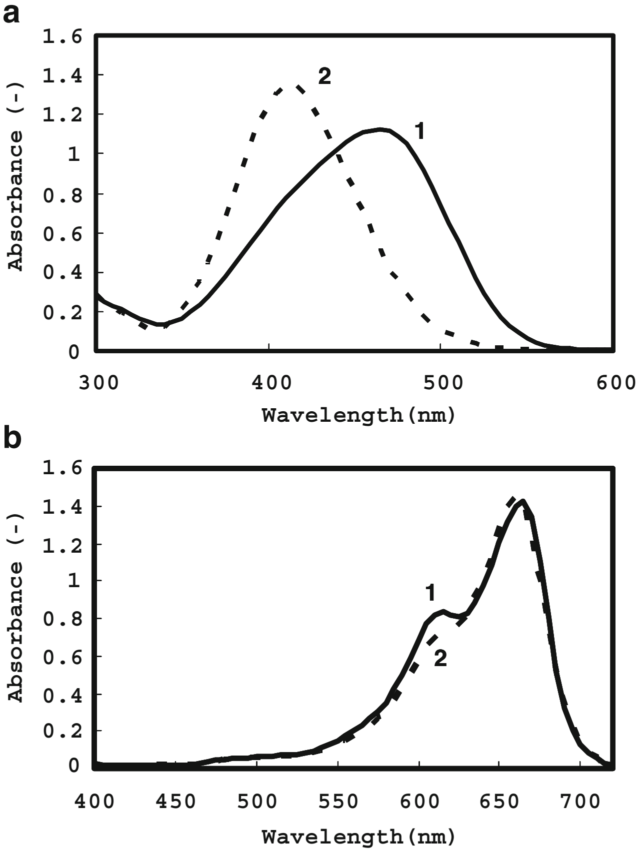

Fig. 6 **a** Absorption spectra of methyl orange in different solvents: *1* water and *2* DG reverse micelles. **b** Absorption spectra of methylene blue in different solvents: *1* water and *2* DG reverse micelles

secondary bound water are low compared to the polarity of free water. Likewise, there might be these types of water in DG reverse micelles. From the results of absorption maxima of dyes, it is suggested that methyl orange and methylene blue are located in bound and free water in DG reverse micelles, respectively.

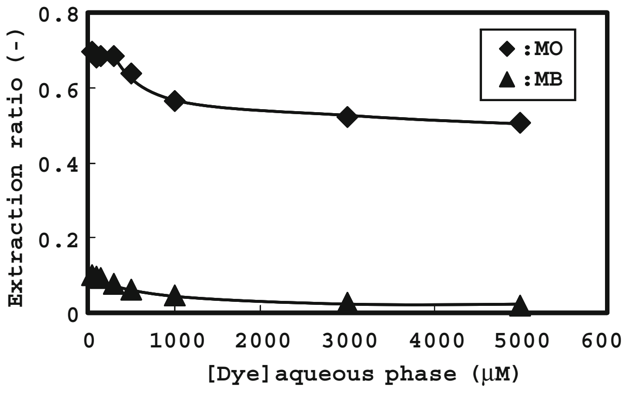

Fig. 7 Dependence of extraction ratios of dyes on the concentration of dyes in an aqueous phase at pH 7. Isooctane/*n*-butanol (7:3 (*v*/*v*)) containing 50 g/L DG was used as an organic phase, while a buffer solution of 0.01 M containing a certain amount of methyl orange (*MO*) or methylene blue (*MB*) was used as an aqueous phase. The extraction was carried out at 25 °C and 120 rpm for 2 h

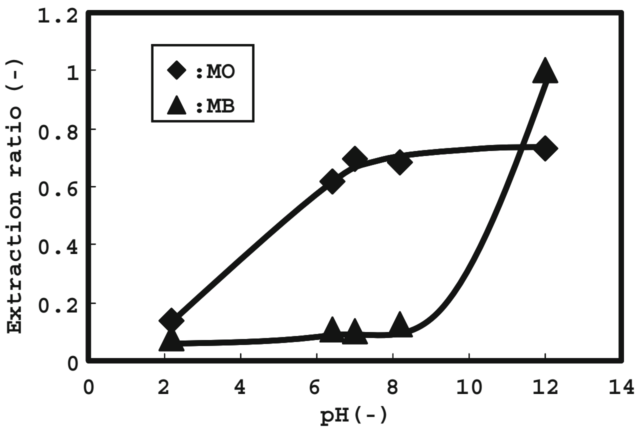

Fig. 8 Effect of the pH of an aqueous phase on extraction ratios of methyl orange and methylene blue. Isooctane/*n*-butanol (7:3 (*v*/*v*)) containing 50 g/L DG was used as an organic phase, while a buffer solution of 0.01 M containing 50 μM methyl orange (*MO*) or methylene blue (*MB*) was used as an aqueous phase. The extraction was carried out at 25 °C and 120 rpm for 2 h

Figure 7 shows the extraction ratios of methyl orange and methylene blue against the concentration of dyes in an aqueous phase at pH 7 and 25 °C before extraction. The

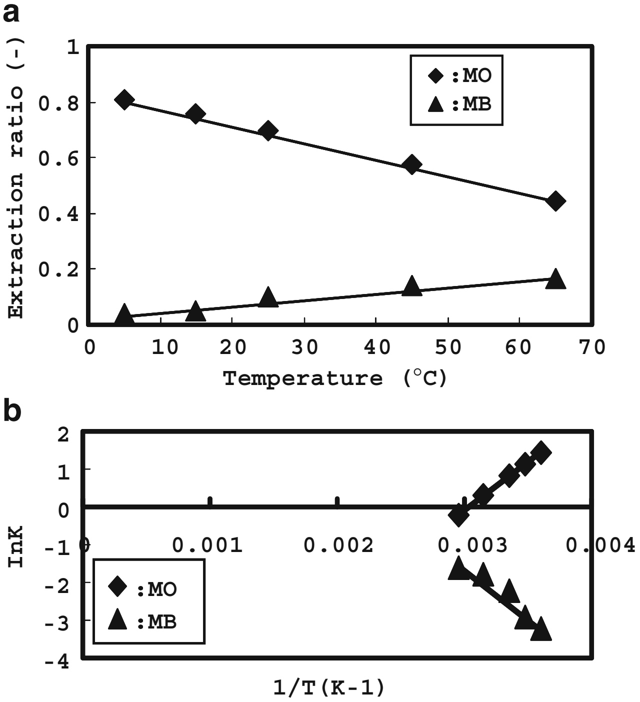

Fig. 9 **a** Relationship between extraction ratios of dyes and temperature at pH 7. **b** ln *K* vs. 1/*T*. Isooctane/*n*-butanol (7:3 (*v*/*v*)) containing 50 g/L DG was used as an organic phase, while a buffer solution of 0.01 M containing 50 μM methyl orange (*MO*) or methylene blue (*MB*) was used as an aqueous phase. The extraction was carried out at 120 rpm for 2 h

extraction ratios of both methyl orange and methylene blue decreased with an increase in the concentration of dyes. At 5,000 μM, the extraction ratio of methyl orange was 0.5, and the extraction ratio of methylene blue was 0.02. Methyl orange and methylene blue were condensed about 14- and 0.6-fold in the water pool of reverse micelles compared to the aqueous phase before extraction, respectively. It is suggested that methyl orange solubilized in DG reverse micelles tend to be located in the vicinity of the interface of reverse micelles since methyl orange has an amphiphilic form when it is deprotonated as shown in Fig. 3. On the other hand, methylene blue may be mainly solubilized in the free water of the water pool due to its ionic character.

Figure 8 shows the effect of the pH of an aqueous phase on extraction ratios of methyl orange and methylene blue at 25 °C. The extraction ratio of methyl orange gradually increased with increasing from acidic pH to neutral pH and was almost constant at alkaline pH, while that of methylene blue was constant until weak alkaline pH and dramatically increased at higher pH. At pH 12, the extraction ratios of methyl orange and methylene blue were 0.73 and 1.0, respectively. Winsor II system was kept stable in the range of pH measured, since DG was specifically robust under alkaline conditions. It seems that the deprotonated form of methyl orange is sufficiently extracted compared to its protonated form due to the amphiphilic nature of the deprotonated form. On the other hand, since the deprotonated form of methylene blue is more ionic than its protonated form, the deprotonated methylene is easily solubilized in the water pool of a reverse micelle at a strong alkaline atmosphere.

Figure 9a shows the effect of extraction temperature on extraction ratios of methyl orange and methylene blue at pH 7. The extraction ratio of methyl orange decreased with increasing extraction temperature while that of methylene blue increased. In the range of temperature examined, the maximal extraction ratio of methyl orange was 0.81 at 5 °C whereas that of methylene blue was 0.17 at 65 °C.

The partition of dyes between aqueous and organic phases is correlated with temperature as

$$\ln K = -(\Delta H^*/RT) + (\Delta S^*/R) \qquad (2)$$

where K is the partition coefficient, which is the ratio of number of moles of dyes in an organic phase to number of moles of dyes in an aqueous phase after extraction, ΔH^* is the standard enthalpy change, ΔS^* is the standard entropy change, and R is the gas constant. As seen in Fig. 9b, a good correlation between ln K and $1/T$ was shown in the cases of both methyl orange and methylene blue. The standard enthalpy changes of methyl orange and methylene blue were −21.5 and 21.9 kJ/mol, respectively. On the other hand, the standard entropy changes of methyl orange and methylene blue were −65.3 and 52.8 J/k·mol, respectively. It has been reported that the hydrodynamic diameter of AOT reverse micelles increases with temperature, and a transition of bound-type to free-type water molecules is enhanced [11, 12]. Consequently, it is suggested that the extraction efficiencies of methyl orange and methylene blue are influenced by a decrease in the bound water and an increase in the free water, respectively.

Conclusion

It has been demonstrated that the DG/isooctane/*n*-butanol/water system forms the stable Winsor II system, which can sufficiently solubilize water into w/o type microemulsions, and achieves extraction of methyl orange and methylene blue. Extraction ratios of both two dyes were strongly dependent upon the pH of an aqueous phase. The extraction ratio of methyl orange exhibited about 0.7 at neutral and alkaline pH, while methylene blue was perfectly extracted at pH 12. The extraction ratio of methyl orange decreased with an increase in temperature, whereas that of methylene blue increased with temperature.

References

1. Reife A, Freeman HS (1996) Environmental chemistry of dyes and pigments edn. Wiley, New York
2. Noritomi H, Ito S, Kojima N, Kato S, Nagahama K (2006) Colloid Polym Sci 284:604
3. Noritomi H, Kowata H, Kojima N, Kato S, Nagahama K (2006) Colloid Polym Sci 284:677
4. Noritomi H, Kojima N, Kato S, Nagahama K (2006) Colloid Polym Sci 284:683
5. Noritomi H, Takasugi T, Kato S (2008) Biotechnol Lett 30:689
6. Singh RP, Swaroop D, Annie K (1999) J Ecotoxicol Environ Monit 9:117
7. Okumura Y (1998) Chuo Suisan Kenkyusho Kenkyu Hokoku 11:113
8. Zhu DM, Wu X, Schelly ZA (1992) J Phys Chem 96:7121
9. Pramanick D, Mukherjee D (1993) J Colloid Interface Sci 157:131
10. Kawai T, Shindo N, Kon-no K (1995) Colloid Polym Sci 273:195
11. Nucci NV, Vanderkooi JM (2005) J Phys Chem B 109:18301
12. Mitra RK, Sinha SS, Pal SK (2008) Langmuir 24:49