การศึกษาการดูดซับของสารลดแรงตึงผิวบนอนุภาคยางธรรมชาติ

Adsorption study of surfactants on natural rubber latex particles

Presented in The 2nd Progress in Advanced Materials: Micro/Nano Meterials and Applications

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บทคัดย่อ

การศึกษาการดูดซับของสารลดแรงตึงผิวบนอนุภาคของยางธรรมชาติ โดยใช้สารลดแรงตึงผิวชนิดที่มีประจุลบ ได้แก่ โซเดียมโดเดคซิลซัลเฟต (SDS) สารลดแรงตึงผิวชนิดที่มีประจุบวก ได้แก่ เซทิลไตรเมทิลแอมโมเนียมโบรไมด์ (CTAB) และสารลดแรงตึงผิวชนิดที่ไม่มีประจุ ได้แก่ ออกทิลฟีนอลพอลีออกซีเอทิรีน (TritonX-100) บนอนุภาคยางธรรมชาติ ไอโซเทอมการดูดซับของสารลดแรงตึงผิวสามารถอธิบายได้ด้วยสมการของ Freundlich พบว่า CTAB สามารถดูดซับบนอนุภาคยางได้มากกว่า SDS และ TritonX-100 ซึ่ง CTAB ดูดซับบนอนุภาคยางได้ด้วยแรงทางไฟฟ้า (Electrostatic interactions) และดูดซับด้วยส่วนที่ไม่มีประจุ (Hydrophobic interactions) เมื่อเปรียบเทียบการดูดซับของ CTAB บนอนุภาคยางกับการดูดซับของ CTAB บนอนุภาคยางที่มี SDS ดูดซับอยู่ พบว่า CTAB ที่ดูดซับบนอนุภาคยางที่มี SDS ดูดซับอยู่สามารถดูดซับได้มากกว่า CTAB ที่ดูดซับบนอนุภาคยาง โดย CTAB เกิดเป็น bilayer อยู่บน SDS ที่ดูดซับอยู่บนอนุภาคยางธรรมชาติ

Abstract

Adsorptions of anionic surfactant (Sodium dodecyl sulphate, SDS), cationic surfactant (Hexa-decyltrimethylammonium bromide, CTAB) and non-ionic surfactant (octylphenolpoly (oxyethylene), TritonX-100) on natural rubber (NR) latex particles were studied. The adsorption isotherms of these surfactants on NR particles were constructed. It was found that CTAB adsorbed more on NR compared with SDS and TritonX-100 adsorption because CTAB molecules can adsorbed on NR surface by electrostatic interactions and hydrophobic interaction. The adsorption of CTAB on NR particles can be enhanced when NR particles was preadsorbed with SDS because the bilayer of CTAB could be formed via tail-to-tail hydrophobic interaction on top of adsorbed-SDS.

คำสำคัญ: สารลดแรงตึงผิว, ยางธรรมชาติ, การดูดซับ
Keywords: Surfactant adsorption, Natural rubber latex, SDS, CTAB, TritonX-100

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1. Introduction

Adsorption isotherm is a plot between surface adsorption amount and equilibrium surfactant concentration in aqueous phase. For surfactant adsorption on strongly charged surface, the adsorption isotherm is typically an S-shape curve which can be separated into four regions: In region I at low surfactant concentration, the surfactant adsorbed mainly by ion-exchange. As the surfactant concentration increased, there is a marked increase of adsorption resulting from interaction of the hydrophobic chains of oncoming surfactant with those of previously adsorbed surfactants and with themselves. In region III, the slope of isotherm is reduced because adsorption now must overcome electrostatic repulsions between the oncoming surfactants and the similarly charge solid surface. Adsorption in this fashion is usually complete in region IV, when the surface is covered with a monolayer or bilayer of the surfactant and micelles are starting to form. Adsorption of surfactant onto hydrophobic surface is different to adsorption on hydrophilic surface. The hydrophobic tail of surfactant is adsorbed on solid surface, so the orientation of the molecules of surfactant is mostly parallel to the surface. When the molecules of surfactant continue to adsorbed on the surface, the orientation is more and more perpendicular to the surface and finally, the hemi-micelles is formed (S.Vijitra, 2003).

The adsorption of different types of surfactant on NR latex particles can provide interesting information about the adsorption mechanism. The surfactant adsorption on NR latex particles can take place by electrostatic interactions via head-to-head and hydrophobic interaction via tail-to-tail.

2. Experimental

2.1. Materials

Concentrated NR latex (60 % rubber content) was purchased from Thai-Hua Company, Thailand. An anionic surfactant, Sodium dodecyl sulfate (SDS), was obtained from APS Ajax Finechem. A cationic surfactant, Cetyl trimethylammonium bromide (CTAB) was purchased from Fluka. Octylphenol poly (oxyethylene) (TritonX-100) was provided by Sigma-Aldrich. Sodium hydroxide (NaOH) with 99% purity was obtained from Merck. Hydrochloric acid (HCl) was obtained from Carlo Erba. Anionic ion-exchange resin (Dowex1X8) and cationic ion-exchange resin (Dowex50WX8) used for NR latex cleaning were obtained from Fluka. Ammonium Hydroxide (NH_4OH) with 30%v/v in water for stabilization of NR latex was obtained from J.T.Baker.

2.2. Purification of NR latex

Concentrated Natural rubber (NR) latex was purified by centrifugation at 10,000 rpm for 20 minutes at 30°C and the upper layer was dispersed in ammonium hydroxide (7% v/v) solution. Afterwards, the resultant NR latex was diluted in DI water to 1% w/w. The diluted latex was mixed with ion-exchange resins and stirred overnight. Then, the ion-exchange resins was filtered out. The conductivity of the latex was measured using conductometer (Thermo Orion model 105 with cell constant=1.023 cm^{-1}). The ion-exchange cleaning process was repeated until the conductivity of the purified NR latex did not change.

2.3. Dynamic Light Scattering

Particles size of NR latex was determined using Dynamic light scattering technique with Brookhaven Instrument B1-9000 particle sizing.

Average particles size and polydispersity index (PDI) were calculated by the following equations:

$$\overline{D_n} = \frac{\sum n_i d_i}{\sum n_i} \quad (1)$$

$$\overline{D_w} = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \quad (2)$$

$$PDI = \frac{\overline{D_w}}{\overline{D_n}} \quad (3)$$

where $\overline{D_w}$ is weight-average particle size, $\overline{D_n}$ is number-average particle size, n_i is number of particle and d_i is particles size (nm).

2.4. Zeta potential

The charge property on NR particle surface can be identified by the zeta potential measurement. NR latex was dispersed in 1 mM NaCl solution and the pH of the dispersion was adjusted by adding either 0.1 M NaOH or 0.1 M HCl. The zeta potential of NR latex was measured at 25°C using Malvern instrument DTS 1060 zetasizer at 25°C

2.5. Adsorption experiment

The various concentrations of surfactants were prepared. Then 10 mL of 1%w/w NR latex was mixed in 25 mL of surfactant solutions. The mixtures were constantly shaken in water bath at 30°C for 78 hrs. The adsorbed NR latex was separated from the free surfactant by centrifugation at 5300 rpm for 100 min. The surfactant concentration was analyzed by refractive index (RI) detector (Waters 2414).

3. Results and discussion

3.1. Particles size of NR particles by Dynamic Light Scattering (DLS)

The particles size distribution of NR latex particles measured by DLS is shown in Figure1. The NR latex particle size was in the range of 150 to 750 nm. The number average particle size $\left(\overline{D_n}\right)$ was 367 nm and the weight average particle size $\left(\overline{D_w}\right)$ was 478 nm. The polydispersity index (PDI) was 1.34 indicating the broad particles size of NR latex.

3.2. Zeta potential of NR latex particles

Figure 2 shows zeta potential of NR latex particles in 1 mM NaCl electrolyte background measuring at different pH at 25 °C. It was found that the negative zeta potential value increased with increasing pH. This is because NR particle surface contain long chain fatty acid soap and polypeptides which provide a natural stabilizer for NR particles (see Figure 3). At high pH, phospholipids on NR surface was hydrolyzed to become long chain fatty acid soap which result in the more negative zeta potential(C. C. HO,T. KONDO, N. MURAMATSU, and H. OHSHIMA, 1996).

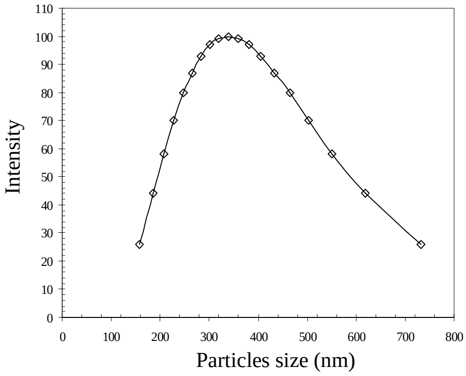

Figure 1. Particles size distribution of NR latex particles measured by dynamic light scattering.

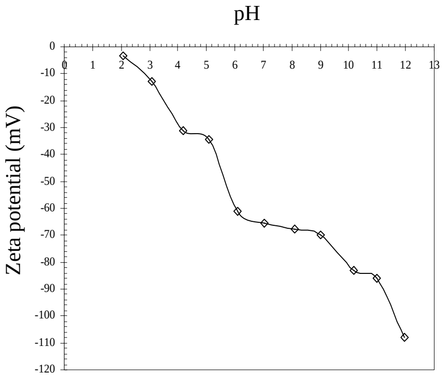

Figure 2. Zeta potential measurement of NR latex particles in 1 mM NaCl at 25°C.

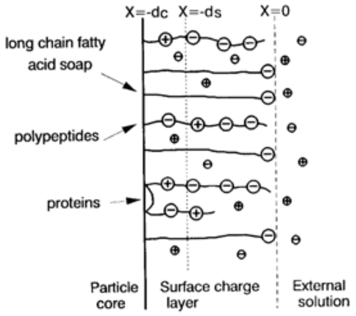

Figure 3. A schematic model for an ion-penetrable layer on NR particle surface (C. C. HO, T. KONDO, N. MURAMATSU, and H. OHSHIMA, 1996).

3.3. Adsorption isotherms of surfactants on NR latex particles

The adsorption isotherms of three different types of surfactant on NR latex particles were displayed in Figure 4. Also shown in Figure 4 is the plot of Langmuir isotherm expressed in equation 4 and Freundlich isotherm expressed in equation 5.

Evidently, Freundlich model provided better fits with the experimental adsorption of SDS, CTAB and TritonX-100 on NR particles.

Langmuir isotherm : $q_e = KC_e/((1/b)+C_e)$ (4)

Freundlich isotherm : $q_e = K_F C_e^{1/n}$ (5)

Where q_e is the amount adsorbed of surfactant at equilibrium (μmol/gNR), C_e is the equilibrium concentration of the surfactant, K and b are Langmuir constants and K_F and $1/n$ are Freundlich constants.

K_F is the adsorption capacity and $1/n$ gives of how favorable the adsorption process(B.H. Hameed, A.T.M. Din, and A.L. Ahmad, 2007). To determine the constant K_F and $1/n$, the log-log plot of q_e and C_e was constructed as shown in Figure 5. The values of K_F and $1/n$ are tabulated in Table 1.

Table 1 Freundlich isotherm constants for SDS, CTAB and TritonX-100 adsorption on NR particles at 30°C

Type of Surfactant	Constants	
SDS	$1/n$	1.40
	K_f	17.31
	R_2	0.99
CTAB	1/n	0.80
	Kf	106.12
	R2	0.99
TritonX-100	$1/n$	1.43
	K_f	26.00
	R_2	0.91

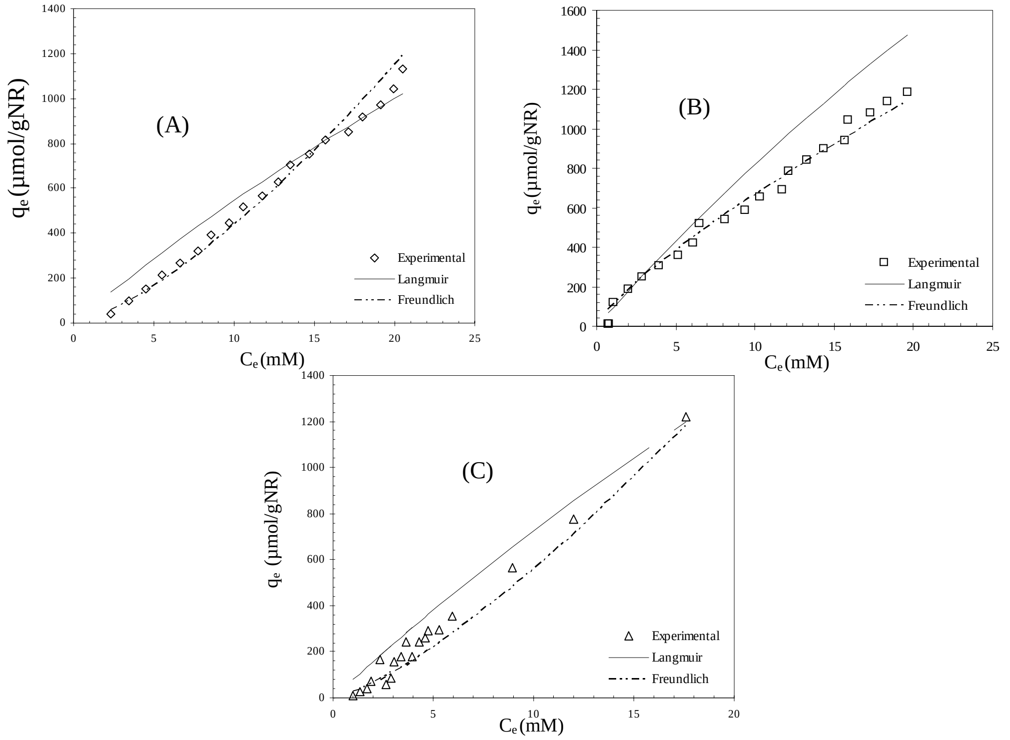

Figure 4. Adsorption isotherm of SDS (A), CTAB (B) and TritonX-100 (C) on NR latex particles at 30°C and pH 9.

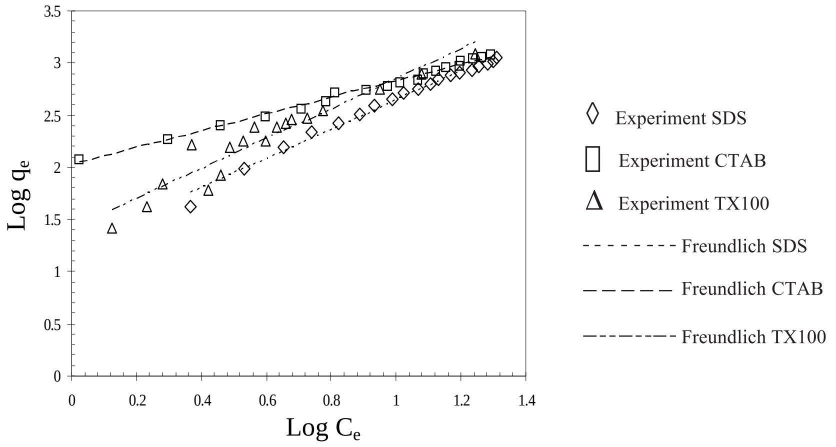

Figure 5. log of adsorbed amount of surfactant (q_e) versus log of the equilibrium surfactant concentration (C_e) for adsorption of SDS, CTAB and TritonX-100 on NR particles.

K_F of CTAB showed a higher value compared with that of SDS and TritonX-100 indicating that CTAB can be adsorbed more on NR particle surface. $1/n$ of SDS and TritonX-100 showed a similar number implying that both were adsorbed on NR particle surface with a same fashion. At low concentration of CTAB, the adsorption can occur through electrostatic interactions between the positive charge CTAB head group and the weakly negative charge of NR particle surface, not only that the tail of CTAB molecules can be adsorbed on uncharged surface of NR particles via hydrophobic interactions. As the CTAB concentration increased, the orientation of CTAB molecules was perpendicular to the surface giving higher adsorption capacity of CTAB than those of SDS and TritonX-100.

The adsorptions of SDS and TritonX-100 on NR particle surface were similar because SDS contains the negative-charge head groups and TritonX-100 contains polar charge head groups. Therefore SDS and TritonX-100 can be adsorbed by hydrophobic interactions between tail groups and uncharged surface of NR particles. At low concentration the orientation of adsorbed surfactant molecules are mostly parallel to the surface. As the surfactant concentration increased, the surfactant molecules orient to perpendicular with the surface and will arrange them self as the hemi-micelles. At high surfactant concentrations.

3.4. Adsorption of CTAB on NR preadsorbed with SDS

Figure 6 shows the adsorption isotherm of CTAB on NR latex particles and CTAB on SDS-adsorbed NR latex particles. Both isotherms can be described by Freundlich isotherm and the constants are tabulated in Table 2.

K_F for CTAB on SDS-adsorbed NR particles is higher than K_F for CTAB on bare NR particles indicating that CTAB can be adsorbed more on SDS-adsorbed NR particles. The $1/n$ showed the similar values for both cases of CTAB adsorption indicating that CTAB adsorbed with hydrophobic and electrostatic interactions. The CTAB adsorption on NR particles which preadsorbed with SDS can occur via the electrostatic interaction as well as the hydrophobic interactions. When the CTAB concentration was increased, first the electrostatic interaction causes the head-to-head adsorption between CTAB and adsorbed-SDS on NR particles. After that, if the CTAB concentration was increased further, the approaching CTAB molecules will from the second layer of CTAB on adsorbed-CTAB through tail-to-tail hydrophobic interaction.

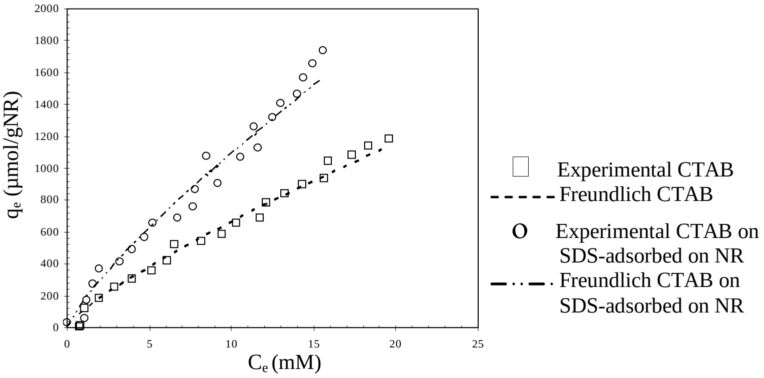

Figure 6. Adsorption isotherm of CTAB on SDS-adsorbed NR latex particles compared with that of CTAB on NR latex particles at 30°C and pH 9.

Table 2 Freundlich isotherm constant for surfactant at 30°C

Adsorption	Constants	
CTAB on NR latex particles	$1/n$ K_f R_2	0.80 106.12 0.99
CTAB on SDS adsorbed NR latex particles	1/n Kf R2	0.81 169.24 0.97

4. Conclusions

Adsorption isotherms of SDS, CTAB and TritonX-100 on NR latex particles can be described by the Freundlich model. CTAB showed a higher adsorption capacity on NR particles than TritonX-100 and SDS because CTAB adsorbed on NR latex particles by electrostatic attractions (head group) and hydrophobic interactions (tail group). The adsorption capacity of CTAB can be enhance by preadsorbed NR latex particles with negative charge SDS.

Acknowledgements

The financial support from Integrated Nanotechnology Research Center, Khon Kaen University (NanoKKU) is acknowledged. The authors would like to thank Department of Chemistry, Khon Kaen University for research facilities and Department of Physics, Khon Kaen University for Dynamic light scattering measurement.

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