

Adsorption Mechanism of Surfactants on Nonwoven Fabrics

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ABSTRACT: For improved surface properties, nonwoven fabrics of polypropylene and poly(ethylene terephthalate) were treated with several kinds of surfactants, including anionic, cationic, and nonionic types. The adsorption isotherms of the anionic, cationic, and nonionic surfactants on the nonwoven fabrics were different. The adsorption isotherm of the cationic surfactant (dodecyl dimethylbenzyl/ammonium chloride) exhibited a maximum. The adsorption isotherm of the anionic surfactant (sodium dodecylbenzene sulfonate) was in the shape of the fifth Brunauer adsorption isotherm, and that of the nonionic surfactant (alkylphenol/ethylene oxide condensate) was similar to the fourth

Brunauer adsorption isotherm. The time of the adsorption equilibrium was constant for the same types of adsorbate and adsorbent, and it was not related to the initial concentration. The specific surface resistance of the nonwoven fabrics decreased substantially after the adsorption of ionic surfactants. The nonwoven fabrics with the surfactants were characterized with scanning electron microscopy and X-ray photoelectron spectroscopy. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3210–3215, 2003

Key words: surfactants; adsorption; poly(propylene) (PP)

INTRODUCTION

With most real surfaces being heterogeneous in nature, their reactivity is determined by the type and distribution of various surface groups and by the micromorphology at the atomic level.¹ Being porous solids, nonwoven fabrics have complicated surface structures. The region of surface irregularities is present for all real surfaces, and this makes it difficult to determine the flow and storage of surfactants in a porous medium.² As a result, it is not easy to clearly understand the adsorption mechanism of surfactants for nonwoven fabrics. Surfactant adsorption onto nonwoven fabrics, which significantly affects their processing and performance, is one important topic to be further investigated.

There have been numerous measurements of surfactant adsorption isotherms. A large variety of methods have been used to evaluate surface properties, but few are universal enough for all systems.³ Adsorption by hydrogen bonding is generally thought to be a possible mechanism, which often forms selective adsorption schemes. In the recent past, the most common method for the exploitation of the surface properties of a target surface involved the use of electrostatic interactions.⁴ A model based on the competitive adsorption of surfactant mixtures exhibits both a maximum and a

minimum, depending on the relative concentration of each surfactant.⁵ Both this model and the mass action model assume that the surfactant monomer interacts with the surface and the micelle competitively. However, this feature is not present in the micellar exclusion model.

To date, there have been some studies of the dynamics of surfactant adsorption for nonwoven fabrics. For example, Trogus et al.⁶ found that a nonequilibrium Langmuir-type isotherm could be used to model the adsorption of alkyl benzene sulfonates on Berea Cores. Ramirez et al.⁷ was involved in similar studies with Triton-X-100. Grow and Shaeiwitz⁸ used a packed bed apparatus to investigate the rates of adsorption of surfactants on solid surfaces. Bisio et al.⁹ ascertained that nonionic and counterionic surfactant adsorption occurred in three regions at a neutral pH. Hodgson and Berg¹⁰ studied wicking flow in random fiber networks for various pure liquids and surfactant solutions. Damania and Bose¹¹ researched the effects of surfactants on the spreading of liquids on solid surfaces. Smorodin and Derjaguin¹² developed the concept of surface phenomena in wetting films on energetically inhomogeneous surfaces of solids. Elaissari et al.¹³ provided methods for studying the adsorption mechanism.

In this experimental study, we chose one or two surfactants from each type of surfactant (anionic, cationic, and nonionic) to study the adsorption mechanism of nonwoven fabrics, the materials of which were polypropylene (PP) and poly(ethylene terephthalate) (PET).

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EXPERIMENTAL

Materials

Nonwoven fabrics of PP and PET were purchased from the Chengdu Textile Factory (Sichuan, China). The main characteristics of the nonwoven fabrics were their thickness (mass per unit area) and the diameter (dtex) of the fibers bonding the nonwoven fabrics. Our samples had the following characteristics:

1. The PP nonwoven fabrics: 13.37 g/m² (0.5 dtex) and 118.54 g/m² (0.5 dtex).
2. The PET nonwoven fabrics: 48.55 g/m² (1.79 dtex), 92.48 g/m² (2.20 dtex), 114.73 g/m² (1.12 dtex), 132.05 g/m² (2.38 dtex), 119.06 g/m² (2.00 dtex), 129.478 g/m² (1.52 dtex), 325.56 g/m² (6.67 dtex), and 603.12 g/m² (5.04 dtex).

The cationic surfactant 1227 (dodecyl dimethylbenzyl/ammonium chloride) and the anionic surfactant LAS (sodium dodecylbenzene sulfonate) were purchased from the Feishang Factory of Special Chemicals (Jiangsu, China). At 25°C, their critical micelle concentration (cmc) values were 1.0 × 10⁻⁴ and 1.5 × 10⁻³ mol/L, respectively. The nonionic surfactant OII-10 (alkylphenol/ethylene oxide condensate) was purchased from Tianjing Fine Chemicals Co. (Tianjing, China); its cmc was 7.6 × 10⁻⁵ mol/L. The nonionic surfactant TX-10 (alkylphenol ethoxylate) was purchased from Jilin Petro-Cemicals Co. (Jilin, China).

The water used in this experiment was thrice distilled, and its pH value was 7.0.

Methods

Capillary-rise method

A surfactant solution with a certain concentration (*c*) was put into a 40-mm glass tube (at 25°C) each time, and then the rising height (*h*) of the solution in a glass capillary with a diameter (*d*) of 0.6 mm was measured with a CGY-65 height-measure apparatus (Shanghai Analyzing Instruments Factory, Shanghai, China).

Surface resistance

First, the nonwoven fabric samples were placed in LAS aqueous solutions, and then they were dried. The surface resistance of the original and treated samples was measured with a ZC36 microcurrent meter (Shanghai No. 6 Ammeter Factory, Shanghai, China). The specific surface resistance (*ρ_s*) of a sample could be calculated from the measured value of the surface resistance and the size of the sample area.

Scanning electron microscopy (SEM)

The adsorbent with adsorbates was observed and photographed with a Hitachi X-650 scanning electron microscope (Hitachi Ltd., Tokyo, Japan).

X-ray photoelectron spectroscopy (XPS)

The contents of the particular elements in the adsorbates were determined with a Noray V4105 X-ray photoelectron spectrometer (Noran Instruments Inc., Middleton, WI).

RESULTS AND DISCUSSION

Adsorption isotherms

Simple and reliable, the capillary-rise method¹⁴ was used to measure the surface tension of the surfactant solutions.

According to the Young–Laplace equation, the static pressure reduced by the liquid height due to the capillary height ΔP equals

$$\Delta P = \frac{2\gamma}{r} \tag{1}$$

where *r* is the capillary radius and γ is the interfacial tension. If *h* is the height from the meniscus to the liquid surface, ΔP is equal to $\Delta\rho gh$, where $\Delta\rho$ is the density difference between the liquid and gas and *g* is the gravity acceleration. Therefore, eq. (1) could be rewritten as

$$a^2 = \frac{2\gamma}{\Delta\rho g} = rh \tag{2}$$

where *a* is the capillary constant.

When the contact angle θ is equal to 0, *a*² can be calculated according to the equation of the Rayleigh progression approximation:

$$a^2 = r \left(h + \frac{r}{3} + \frac{0.1228r^2}{h} + \frac{0.1312r^3}{h^2} + \dots \right) \tag{3}$$

By the resolution of eqs. (2) and (3), γ can be calculated, and the γ -*c* curve can be plotted.

After nonwoven fabrics were placed into surfactant solutions, the value of *h* was recorded when the surfactant adsorption onto the surface arrived at an equilibrium. The value of γ was calculated according to eqs. (2) and (3), and the value of *c* was obtained through the experimental γ -*c* curve. According to the mass balance equation, we have

$$n_2^s = \frac{\Delta n_2}{m} = \frac{V(c_0 - c)}{m} \tag{4}$$

where *n*₂^s (mol/g) is the adsorbate quantity on 1 g of the adsorbent, Δn_2 (mol) is the adsorbed quantity, *m* (g) is the mass of an adsorbent, *V* (L) is the volume of the solution, *c*₀ (mol/L) is the concentration of the solution before adsorption, and *c* (mol/L) is the con-

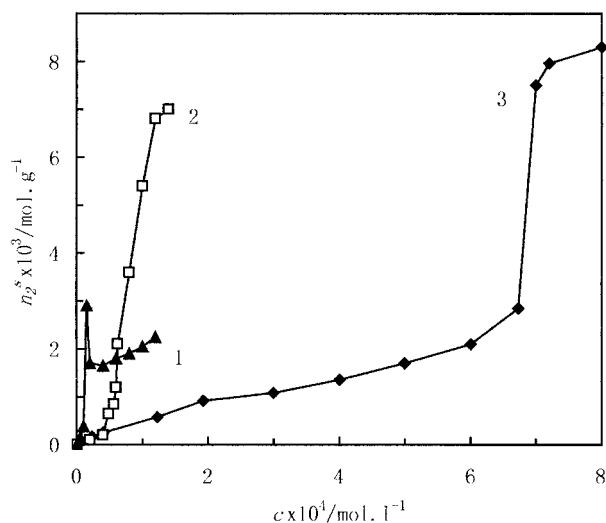


Figure 1 Surfactant adsorption isotherms of PET non-woven fabrics (at 25°C): (1) 1227 aqueous solution, (2) LAS aqueous solution, and (3) OII-10 aqueous solution.

centration of the solution after adsorption. Therefore, the surfactant adsorption isotherm was plotted.

As shown in Figure 1(1), the adsorption isotherm of the cationic surfactant 1227 rises sharply with its concentration increasing. However, after experiencing the maximum point, the adsorption isotherm descends rapidly and then gradually increases again. At the beginning, the strong static effect between the cationic surfactant 1227 and the negative surface of PET non-woven fabrics in a pH 7 aqueous solution results in the adsorption quantity remarkably increasing. With the adsorption through the two regions⁹ (region I is below the cmc and region II is near the cmc), the adsorption changes from monolayer adsorption by lying prone to the solid surface to standing vertical, with the hydrophobic moiety exposed to the aqueous solution; this results in the solid-liquid interface with identical electrical charges and the adsorption quantity decrease. Very slightly beyond the cmc, region III commences with tail-tail bilayer adsorption, so the adsorption isotherm rises again. The cationic surfactant 1227 is not perfectly pure. Perhaps this causes the maximum on its adsorption isotherm.¹⁵ The main reason for the minimum on the adsorption isotherm is the rearrangement and disadsorption of cationic surfactant 1227 molecules on the fibers.

The second curve shows that the adsorption isotherm of anionic surfactant LAS is in the shape of the fifth Brunauer adsorption isotherm.¹⁶ At a low concentration, multilayer adsorption forms and results in capillary adsorption with increasing concentration, and at a higher concentration, the adsorption quantity tends to a limited value. This kind of adsorption isotherm shows that the interaction between two adsorbate molecules is stronger than that between an ad-

sorbate molecule and an adsorbent molecule. This means that porous adsorbents have stronger adsorption ability.

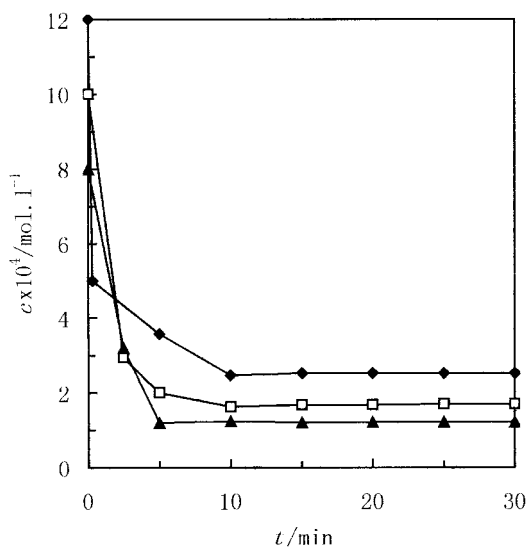
The third curve confirms that the adsorption isotherm of nonionic surfactant OII-10 is similar to the fourth Brunauer adsorption isotherm. At a low concentration, because of the monolayer adsorption, the pore structure of the adsorbent appears to be capillary adsorption with the concentration increasing, and the adsorption quantity goes up dramatically until the capillary pores of the adsorbent are full of adsorbents. Then, the adsorption quantity remains nearly constant, and the adsorption of adsorbents becomes multilayer until adsorption equilibrium. The reason may be that the interaction between the nonionic surfactant molecules is weak.

Change in the equilibrium concentration with the adsorption time

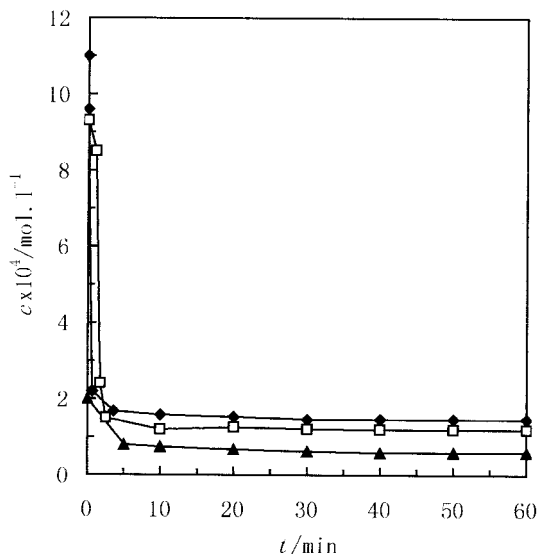
Figure 2 indicates that adsorption equilibrium can be achieved after a long period of time and that the time is almost constant for the same kinds of adsorbate and adsorbent. The reason is that the adsorption from the solution is too much slower than that from air. The main factor that decides the adsorption velocity is the comparative size between the adsorbate molecule and the pores of the adsorbent. Most of the surface of a porous solid is the inner-pore surface, which is the primary part contributing to adsorption. Adsorbate molecules can only be adsorbed after they pass through pore passages and spread into inner pores. The size of a pore is the key factor for the same adsorbate, so the adsorption equilibrium time is definite for the same surfactant and adsorbent, which is irrelevant to the initial concentration (c_0). Because the special blocks of LAS and OII-10 molecules are smaller than those of 1227 molecules (see the configuration of the molecular formulas of LAS, OII-10, and 1227 molecules), LAS and OII-10 molecules can easily enter the pore passages, that is, spread more quickly. Therefore, the time for the adsorption equilibrium of LAS and OII-10 is shorter than that of 1227.

Specific surface resistance

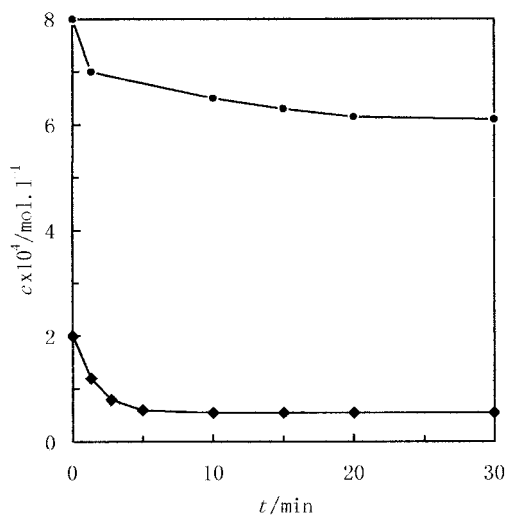
Table I lists the ρ_s values (Ω) of various nonwoven fabrics before and after the surface treatment by LAS aqueous solutions with a concentration of 2.74×10^{-4} mol/L for 5 min. The data in Table I show that ρ_s of nonwoven fabrics with the adsorbate decreases much more than that of fabrics without the adsorbate. In particular, ρ_s of superfine PP decreases about 2 orders of magnitude after the surface treatment. This result clearly proves that surfactant adsorption occurs, which increases surface electronic charges and reduces ρ_s . It is reasonable that the surface properties of



(a)



(b)



(c)

TABLE I
 ρ_s/Ω Values of Various Nonwoven Fabrics Before and After Surface Treatment by an LAS Aqueous Solution

Samples	Before	After
0.5 dtex(13.37g/m ²)PP	2.37×10^{13}	2.25×10^{11}
0.5 dtex (118.54g/m ²) PP	3.35×10^{10}	2.60×10^8
1.12 dtex (114.73g/m ²) PET	1.63×10^{11}	3.02×10^9
1.52 dtex (129.47g/m ²) PET	5.71×10^{11}	3.01×10^{10}
1.79 dtex (48.55g/m ²) PET	1.34×10^{11}	3.27×10^9
2.00 dtex (119.06g/m ²) PET	3.59×10^{11}	6.12×10^9
2.20 dtex (92.48g/m ²) PET	3.02×10^{11}	4.25×10^9
2.38 dtex (132.05g/m ²) PET	2.53×10^{12}	1.43×10^{11}
5.04 dtex (603.12g/m ²) PET	5.88×10^{11}	2.78×10^{11}
6.67 dtex (329.56g/m ²) PET	2.04×10^{12}	3.27×10^{11}

nonwoven fabrics are changed by surfactant adsorption.

SEM photographs

Surfactants are mainly adsorbed at the intersection of fibers, as shown in Figure 3. When a sample is immersed in a surfactant solution without outer force, the permeation of water achieves equilibrium by water filling in the fabric pores. For adsorption processes in porous media, the energy of solute/sorbent interactions governs the solute distribution between the interfacial zone and the liquid phase.⁴ However, the size of pores is always heterogeneous. When the sample is placed in a dryer after immersion and the solvent vaporizes, surfactants separate from big pores and remain on the surfaces of fabrics or fibers. Because the capillary pressure of small pores is higher, the remainder of the liquid with dissolved or separated surfactants seeps into narrow pores during vaporization. Generally, the smallest pores distribute deeply inside fibers, so surfactants deposit in the smallest pores. During the process of drying, the capillary pressure induces the movement from liquid bulk to a vaporization surface and at the same time brings dissolved or small surfactant grains moving to the surface. If the size of the surfactants is similar to that of the fabric pores, surfactant grains will accumulate on the surfaces of nonwoven fabrics. The molecular sieve effect is enhanced by the attractive force between the textile surface and surfactant grains.⁶

Figure 4 shows the layer of surfactants adsorbed around the fibers. As PET and PP are nonionic adsorbents, surfactants often make their hydrophobic parts accessible to the adsorbent surface, and their hydro-

Figure 2 Change in the equilibrium concentration (c) with the adsorption time (t): (a) 1227 [(\blacklozenge) $c_0 = 1.2 \times 10^{-4}$, (\square) $c_0 = 1.0 \times 10^{-4}$, and (\blacktriangle) $c_0 = 8.0 \times 10^{-5}$], (b) LAS [(\blacklozenge) $c_0 = 1.12 \times 10^{-3}$, (\square) $c_0 = 9.6 \times 10^{-4}$, and (\blacktriangle) $c_0 = 2.0 \times 10^{-4}$], and (c) OII-10 [(\bullet) $c_0 = 8.0 \times 10^{-4}$ and (\blacklozenge) $c_0 = 2.0 \times 10^{-4}$].

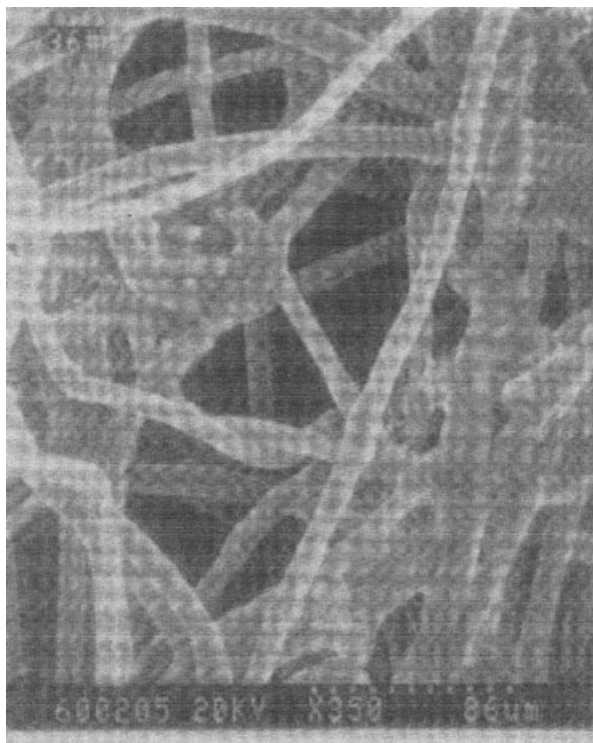


Figure 3 SEM photograph of 0.5-dtex (13.37 g/m²) PP nonwoven fabrics with 10% TX-10.

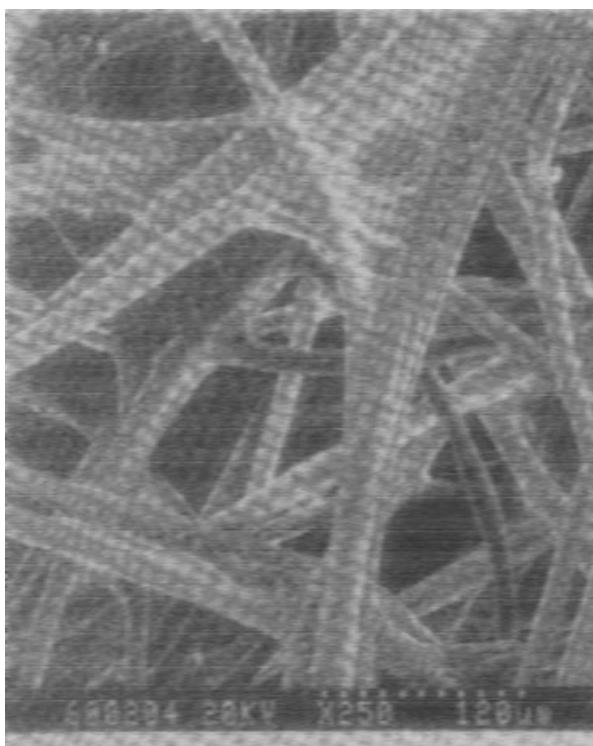


Figure 4 SEM photograph of 1.79-dtex (48.55 g/m²) PET nonwoven fabrics with 10% TX-10.

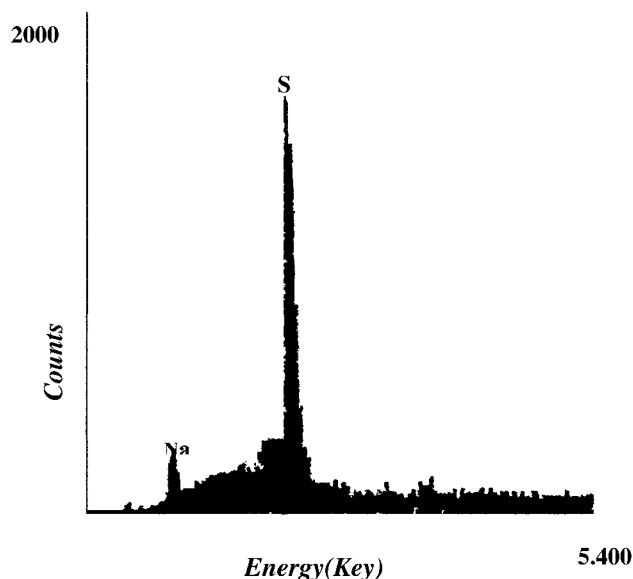


Figure 5 XPS spectrum of 6.67-dtex (329.56 g/m²) PET nonwoven fabrics with 10% LAS.

philic ends are directed toward the solution during absorption onto PP and PET. Therefore, an original nonionic surface is gradually changed into a hydrophilic polarity surface with adsorption proceeding. When the concentration of a surfactant is equal to the cmc, the adsorption quantity of the surfactant comes to a maximum.

However, the adsorption patterns cannot be affirmed from the pictures because the surfactant adsorption from surfactant aqueous solutions onto nonwoven fabrics includes many complicated adsorption patterns in the system. Some adsorption is Langmuir adsorption, but at the same time, multilayer or colloid patterns also exist.¹⁵

Elemental analysis by XPS

Figure 5 illustrates that there is a sodium element and a sulfur element in the samples of PET nonwoven fabrics after LAS is absorbed. This proves that the adsorption of LAS onto the nonwoven fabrics really occurs.

CONCLUSIONS

1. The adsorption isotherms of anionic, cationic, and nonionic surfactants on nonwoven fabrics are different. The adsorption isotherm of cationic surfactant 1227 has a maximum value. The adsorption isotherm of anionic surfactant LAS is in the shape of the fifth Brunauer adsorption isotherm, and that of the nonionic surfactant OII-10 is similar to the fourth Brunauer adsorption isotherm.

2. Adsorption needs time to achieve equilibrium. The main factor deciding the adsorption rate is the comparative size between surfactant molecules and adsorbent pores. The time of adsorption equilibrium is constant for the same types of adsorbate and adsorbent and is not related to the initial concentration.
3. The ρ_s value of nonwoven fabrics after the ionic surfactants are absorbed decreases, so the adsorption on the surface occurs and the surface property changes.
4. Surfactants adsorbed onto the surfaces of nonwoven fabrics are arrayed in a fixed orientation and are primarily centralized at the intersection of fibers.

References

1. Ottaviani, M. F.; Tomatis, M.; Fubini, B. *J Colloid Interface Sci* 2000, 224, 169.
2. Neogi, P.; Miller, C. A. *J Colloid Interface Sci* 1983, 92, 338.
3. Meziani, M. J.; Zajac, J.; Dourllord, J. M.; Jones, D. J.; Partyka, S.; Roziere, J. *J Colloid Interface Sci* 2001, 233, 219.
4. Bjelopavlic, M.; Singh, P. K.; El-Shall, H.; Moudgil, B. M. *J Colloid Interface Sci* 2000, 226, 159.
5. Trogus, F. J.; Schechter, R. S.; Wade, W. H. *J Colloid Interface Sci* 1979, 70, 293.
6. Trogus, F. J.; Schechter, R. S.; Wade, W. J. *Soc Pet Eng J* 1977, 17, 337.
7. Ramirez, W. F.; Shuler, P. J.; Friedman, F. *Soc Pet Eng J* 1980, 20, 430.
8. Grow, D. T.; Shaeiwitz, J. A. *J Colloid Interface Sci* 1982, 86, 239.
9. Bisio, P. D.; Cartledge, J. G.; Keesom, W. H.; Radke, C. J. *J Colloid Interface Sci* 1980, 78, 225.
10. Hodgson, K. T.; Berg, J. C. *J Colloid Interface Sci* 1988, 121, 22.
11. Damania, B. S.; Bose, A. *J Colloid Interface Sci* 1986, 113, 321.
12. Smorodin, V. Y.; Derjaguin, B. V. *J Colloid Interface Sci* 1991, 142, 272.
13. Elaissari, A.; Haouam, A.; Huguenard, C.; Pefferkorn, E. *J Colloid Interface Sci* 1992, 149, 68.
14. Adamson, A. W. *Physical Chemistry of Surfaces*; Wiley: New York, 1976; Chapter 1.
15. Liang, M. L. *Surfactants and Detergent—Preparation, Properties and Practice (in Chinese)*; Science and Technology: Beijing, 1990; p 279.
16. Chen, J. Q.; Dai, M. G. *Colloid Chemistry (in Chinese)*; Higher Education: Beijing, 1984; p 65.