The effect of surfactants on chemical development of ion track nanopores in polymer

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Abstract. The use of surfactants in etching of the track membranes (TMs) enables one to control the pore shape in TMs. This technique is useful to improve flow rate, and to optimize the retention and permeation properties of TMs. The addition of an anionic surfactant, sodium dodecyl diphenyloxide disulphonate (SDDD), to etching solutions leads to the highly tapered pore shape in TMs of the polyethylene terephthalate (PET). To understand the mechanism of the surfactant effect on track etching in the nanometer range, we study the diffusion and adsorption of SDDD on non-etched non-porous, etched non-porous and etched porous PET films. The comparison of non-etched non-porous and etched non-porous films shows the effect of negatively charged surface on the adsorption of surfactant. The comparison of etched non-porous and etched porous PET films shows the different adsorption on film surface and inner wall of nanopore, thus the influence of curvature of the surface on the adsorption of surfactant molecules.

1. Introduction
The nano and micro pores with controlled size and shape are important for variety of applications, such as the micro and ultra filtration membranes, molecular sensors, optical filters, template synthesis of nanotubes and nanowires, nano and microfluidics, etc. [1]. For usual production of TMs, a polymer film is irradiated with the heavy ion beams, and gets the linear traces of damage. Then chemical etching is performed with alkaline aqueous solution to get the pores along the traces. TMs of polymer film usually give cylindrical pore channels. However addition of an anionic surfactant, sodium dodecyl diphenyloxide disulphonate (SDDD) to the alkali solution leads the pore channels to the highly tapered pore profile [2].

Previous works suggest a model as follows [2]-[4]. The chemical etching performed with surfactant decreases the etching rate of the film surface because the adsorption layer of SDDD protects the film surface from hydroxide ions (alkali). However the etching rate of inner wall of pores does not decrease at the first stage because the molecule of SDDD is too large to enter inside of pore and to construct the adsorption layer on inner wall of pores. As the result, highly tapered pores (“cigar-like”) are produced.

For better understanding of these phenomena, we carry out the present work. Goals of the present work are, to measure adsorption isotherms of SDDD on PET films, to study effect of electrolyte...
concentration on the adsorption isotherms, to compare adsorption of SDDD on flat surface and on the pore walls of different curvature.

2. Experimental
PET films (thickness 20µm) were used as the substrate. The three kinds of pre-treatment were performed on the PET films: non-etched non-pore film (NENP, pristine PET film), etched non-pore film (ENP, PET film etched with alkali), etched pore film (EP, PET film irradiated with heavy-ion and etched with alkali). In fig.1 we show the SEM image of an etched pore film which has the pore diameter of 260 nm and pore number of 4.8*10^8 cm^-2. Sodium dodecyl diphenyloxide disulphonate (SDDD) was used for adsorption experiments. The chemical structure of SDDD is shown in Fig. 2. This is an anionic surfactant which has two negatively charged groups in hydrophilic head. The experimental procedure is also shown in Fig.2. Adsorption experiments were performed at room temperature. Small pieces of PET film were put into the SDDD aqueous solution of the concentration C_o. After 24 hours, the PET films were removed and the concentration of SDDD solution C_eq was measured by UV spectrophotometer. From the difference between C_eq and C_o, we found the adsorption of SDDD on the PET films. For NENP and ENP firm, the surface area means two sides of film surfaces (up and bottom sides). For EP film, the surface area is sum of two film surfaces and inner wall of pores.

3. Results
Fig. 3 left shows the influence of the electrolyte KCl concentration on the adsorption isotherm of SDDD on NENP films. Fig.3 right shows the average area occupied by SDDD molecule on NENP film surface. The lines in Figures show the results of fitting by Langmuir formula V= K C_eq V_max / (1+K C_eq). Here, K - Langmuir equilibrium constant, C_eq - the aqueous concentration, V - the amount adsorbed, and V_max - the maximum amount adsorbed as C increases. It shows the higher concentration of KCl leads to the higher adsorption of SDDD on NENP films.

Fig.4 left shows the influence of the electrolyte KCl concentration on the adsorption isotherm of SDDD on ENP film. Fig.4 right shows the average area occupied by SDDD molecule on ENP film. The same as the case of NENP film, the higher concentration of KCl leads to the higher adsorption of SDDD on ENP films.

Fig.5 left shows the influence of the electrolyte KCl concentration on the adsorption isotherm of SDDD on EP-b film. Fig.5 right shows the average area occupied by SDDD molecule on EP-b film. We observed that the adsorption of SDDD on EP-b film is significantly lower than the cases of NENP and ENP films at the same concentration of KCl. It suggests that the adsorption onto the inner walls of

Fig.1 SEM image of the etched-pore film (EP-b) surface. The pore diameter is 260 nm.
Fig.2 The chemical structure of SDDD and the experimental procedure.
pores is lower than the adsorption onto the film surface. We also found that there is practically no adsorption of SDDD in the absence of electrolyte. And this result was same even for EP films which have pores as large as 1000 nm in diameter. (The result is not shown here.)

Fig. 3 Left - The influence of the electrolyte KCl concentration on the adsorption isotherm of SDDD on NENP film. No KCl - diamonds, 0.1M KCl - squares, 1.0M KCl – deltas. Right - The average area occupied by SDDD molecule on NENP film surface. The lines in Figures show the results of fitting by Langmuir formula $V = K \cdot C_{eq} \cdot V_{\text{max}} / (1 + K \cdot C_{eq})$. $K$ - Langmuir equilibrium constant, $C_{eq}$ - the aqueous concentration, $V$ - the amount adsorbed, and $V_{\text{max}}$ - the maximum amount adsorbed as $C$ increases.

Fig. 4 Left - The influence of the electrolyte KCl concentration on the adsorption isotherm of SDDD on ENP film. No KCl - deltas, 0.1M KCl - squares, 1.0M KCl - diamonds. Right - The average area occupied by SDDD molecule on ENP film.
Fig.5 Left - The influence of the electrolyte KCl concentration on the adsorption isotherm of SDDD on EP-b film. No KCl - deltas, 0.1M KCl - squares, 1.0M KCl – diamonds, 3.0M KCl – circles. Right - The average area occupied by SDDD molecule on EP-b film.

Fig.6 shows the adsorption isotherms of SDDD on EP films with different sizes and pore shapes. The electrolyte KCl concentration of SDDD aqueous solution is 0.1M. EP-a has the highly tapered pores which are produced by the chemical etching with SDDD. The effective pore diameter found from gas flow is 280 nm, while the pore diameter at the film surface is about 100 nm. EP-b, EP-c and EP-d have almost cylindrical pores which are slightly tapered towards the depth. Their pore diameters are 260 nm, 480 nm and 1020 nm, respectively. Fig.6 shows that all porous substrates have almost same dependence of SDDD adsorption at 0.1M KCl.

4. Conclusions

The experiments clearly show that the adsorption of anionic surfactant in 260 nm pores is significantly lower than that on flat surface of both etched and non-etched PET film. This phenomenon is quite surprising and needs further investigation. It was also shown that the higher concentration of KCl leads to the higher adsorption of anionic surfactant on all three kinds of PET films (non-etched, etched non-porous, etched porous). Repulsion between the negatively charged sulfonate groups of surfactant molecules seems to be neutralized by the addition of electrolyte KCl. As a result, the anionic surfactant forms denser adsorption layer.

The results obtained are important: (i) for efficient control over the structural characteristics of track membranes; (ii) for better understanding of the processes of adsorption and diffusion of ions and molecules in nanocapillaries with electrical charge on the walls.

References
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