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Displacement of Polymers by Displacers. 2. Poly(ethylene oxide) at the Silica Surface

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ABSTRACT: Displacement of preadsorbed poly(ethylene oxide) (PEO) was examined by adding various displacer molecules, such as methyl cellosolve, dioxane, acetone, and benzene, to a nonporous Aerosil 130 silica in carbon tetrachloride, using a FT/IR spectrometer. The displacement behavior was followed by the adsorbed amount of PEO and IR spectra of the sedimented silica on which PEO and displacers are adsorbed. The critical volume fraction $\phi_{cr}{}^{d}$ of displacer was obtained by extrapolation of the displacement isotherm curve to no adsorbed amount of PEO. The magnitude of $\phi_{cr}{}^{d}$ values increases in the order of methyl cellosolve, dioxane, acetone, and benzene. Except for methyl cellosolve, in other displacers, PEO can be adsorbed at the silica surface. The adsorption-free energy parameter, χ_s, of PEO for these displacers can be evaluated by using a relationship derived by Cohen Stuart, Fleer, and Scheutjens. Large evaluated χ_s values mean that PEO molecules are strongly attached to the silica surface via hydrogen bonding between surface silanol groups and the oxygen atoms in the ethyloxy segments of PEO.

Introduction

Displacement of the preadsorbed polymer chains from solid–liquid interfaces by the addition of low molecular weight displacer molecules has been related not only to practical view points, such as steric stabilization of colloidal particles upon desorption of polymer chains and adsorption chromatography, but also to the evaluation of segmental adsorption free energy, $\chi_s kT$, where k is the Boltzmann constant and T is the absolute temperature. The value of the adsorption free energy parameter, χ_s, was defined by Silberberg[1] in 1968

$$\chi_s = \frac{[\epsilon_{2s} - \epsilon_{1s} + \frac{1}{2}(\epsilon_{11} - \epsilon_{22})]}{kT} \qquad (1)$$

where the term ϵ represents the binary interacting energy among polymer segments (2), solvent molecules (1), and adsorbent surface (s). The χ_s value relates well to the adsorption strength between polymer segments and adsorbent surface. Actually, evaluating the χ_s value leads to further development in the theoretical works on polymer adsorption and quantitatively predicts the adsorption behavior.

In our previous paper,[2] we displaced homodisperse polystyrenes (PS) by various displacers at the silica surface. Moreover, we have proposed a simple route for evaluation of the χ_s value, using eq 2 predicted by Cohen Stuart et al.,[3] if we select a good combination of two solvents, that is, one behaves as a solvent and another as a displacer:

$$\chi_s^{pd} = \ln \phi_{cr}{}^{d} + \chi_{sc} - \lambda_1\chi^{pd} - (1 - \phi_{cr}{}^{d})(1 - \lambda_1)(\chi^{po} - \chi^{pd} - \chi^{do}) \qquad (2)$$

where χ_s^{pd} is the adsorption energy parameter of a polymer segment adsorbing from a displacer molecule, $\phi_{cr}{}^{d}$ is the critical volume fraction of a displacer, χ_{sc} is the critical adsorption energy parameter (polymer adsorption takes place if the χ_s parameter exceeds the χ_{sc} value), λ_1 is the lattice parameter, and χ^{po}, χ^{pd}, and χ^{do} correspond to the interaction parameter between polymer and solvent (po), polymer and displacer (pd), and displacer and solvent (do), respectively.

In this paper we estimate the χ_s parameter of poly(ethylene oxide) (PEO) in various solvents from the displacement of preadsorbed PEO with a narrow molecular weight distribution at a silica surface by the addition of the solvents using eq 2. Moreover, we will discuss the preferential adsorption of PEO over PS at the silica surface for the competitive and displacement adsorption between two polymers[4] based on comparison of the χ_s values for PEO and PS.

Experimental Section

Material. A PEO sample having $M_w = 39 \times 10^3$ and polydispersity index $M_w/M_n = 1.07$ was purchased from Tosoh Co.

Carbon tetrachloride (CCl_4) used as a solvent was distilled just before use.

Spectroquality benzene, dioxane, acetone, and methyl cellosolve were used as displacers without further purification.

The nonporous Aerosil 130 silica (Degussa A. G., West Germany) used as an adsorbent was cleaned by the same procedure as described previously.[5]

Adsorption and Displacement of PEO. The adsorption isotherm of the PEO sample was determined in a 50-mL stoppered glass centrifuge tube containing 0.16 g of silica and 20 mL of a PEO–CCl_4 solution of known concentration, C_0. The mixture in the tube was stirred with a magnetic chip for 24 h to attain equilibrium in an incubator controlled at 35 ± 0.1 °C. The silica suspensions were centrifuged at 3000 rpm for 10 min to sediment the silica using a Kubota KR-200B centrifuge, and the supernatant was carefully withdrawn. The concentration of unadsorbed PEO remaining in the supernatant solution was determined from an

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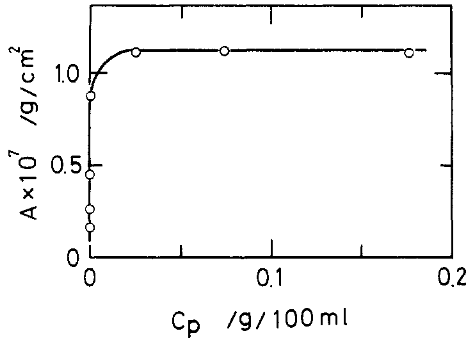

Figure 1. Adsorption isotherm of PEO at a nonporous Aerosil 130 silica in CCl_4.

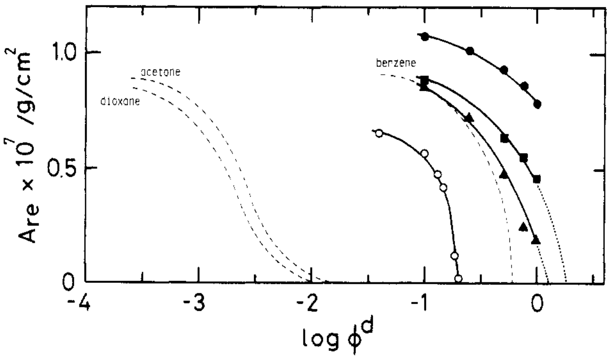

Figure 2. Displacement isotherms of PEO for various displacer molecules: (○) methyl cellosolve; (●) benzene; (□) acetone; (▲) dioxane. Dashed lines indicate the displacement isotherms of PS for benzene, acetone, and dioxane in CCl_4.

IR band at 2890 cm^{-1} due to the CH stretching vibration[4,6] using a JASCO IR-3 type FT-IR spectrometer.

The displacement of PEO by the addition of displacer molecules occurred as follows: (1) PEO molecules were first adsorbed onto silica (0.16 g) from 20 mL of a CCl_4 solution in which the PEO concentration (0.2 g/100 mL) was chosen to be in the plateau region of the PEO adsorption isotherm; (2) after agitation for 24 h at 35 °C and centrifugation, the desired amount of the supernatant solution was withdrawn, and the same volume of displacers or a mixture of displacer and solvent was added; (3) the mixture was agitated again for 24 h at 35 °C; and (4) after centrifugation and evaporation of the CCl_4 and displacer, the residue was dried under vacuum and dissolved in a definite volume of CCl_4 and the concentration of PEO in the supernatant was determined by IR spectroscopy.

The volume fraction of displacer in the mixture was designated as ϕ^d. The volume fraction of displacer in the mixture was designated as ϕ^d. The volume fraction of displacer in the solvent mixture after displacement should be less due to the transfer of displacer to the silica surface. In this paper, the term ϕ^d indicates the dosage volume fraction of the displacer.

To confirm the reproducibility of experiments, we performed at least two experiments for the same concentrations. The errors in the adsorbed amounts are less than 5%.

Results and Discussion

Figure 1 shows the adsorption isotherm of PEO. The adsorption isotherm rises steeply with increasing C_p of the supernatant solution and reches a plateau. The adsorption isotherm is of the high-affinity type, which is characteristic of the adsorption of monodisperse polymers. All PEO molecules adsorb on the silica surface below the initial dosing concentration $C_0 = 0.1$ g/100 mL. This adsorption isotherm is the same as that previously reported.[4] Our previous study showed that the shape of the PEO adsorption isotherm is independent of the molecular weight of PEO.[4]

Figure 2 shows displacement isotherms, i.e., a plot of the remaining amount, A_{re}, for preadsorbed PEO against the logarithm of the volume fraction of displacer molecules. The A_{re} value rather steeply decreases with log ϕ^d and eventually reaches zero at a given ϕ_{cr}^{d}. Above ϕ_{cr}^{d}, all preadsorbed PEO molecules are completely desorbed from the silica surface. The ϕ_{cr}^{d} value is obtained from the displacement isotherm of an extrapolation of the A_{re} value to zero. The ϕ_{cr}^{d} values should contain some artificial errors when we extrapolate the displacement isotherm curve into the region $\phi^d > 1$. It seems to be particularly difficult to extrapolate the curve of the displacement isotherms for benzene. Here we assumed that the extrapolated curve of the displacement isotherms for other displacers do not have a long tail and we obtained $\phi_{cr}^{d} = 0.19_5$, 1.1_5, and 1.8_2 for methyl cellosolve, dioxane, and acetone, respectively by fitting the data points on a polynomial function. Except for the displacement isotherm for methyl cellosolve the ϕ_{cr}^{d} value exceeds 1. This means that PEO molecules can be adsorbed onto the silica surface from benzene, acetone, and dioxane solution. The equilibrium and plateau adsorbed amounts of PEO in the corresponding solvents are plotted at $\phi_{cr}^{d} = 1.0$ in Figure 2. To emphasize the strong adsorption of PEO at the silica surface, the displacement isotherms[2] of PS benzene, dioxane, and acetone in the CCl_4 solvent are shown by dashed lines in Figure 2.

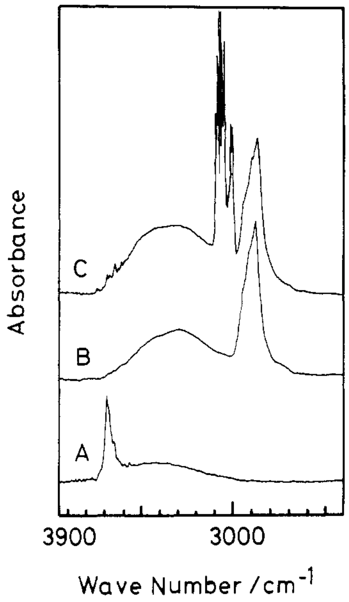

Figure 3. IR spectra of the sedimented silica: (A) silica immersed in CCl_4; (B) silica on which only PEO adsorbs; (C) silica on which PEO and benzene adsorb at $\phi^d = 0.75$.

On the other hand, the desorption process of the preadsorbed PEO molecules by displacer molecules can be followed by the differential IR spectra of the sedimented silica on which PEO and displacers are adsorbed. A typical example is shown in Figure 3: (A) an IR spectrum of the silica immersed in CCl_4 has a band at 3675 cm^{-1} due to the free silanol groups; (B) an IR spectrum of the silica on which PEO molecules are adsorbed in the plateau region of the individual adsorption of PEO has a strong and wide peak at 3300 cm^{-1} for a hydroxy group perturbed by the hydrogen bond between silanol and the oxygen of the adsorbed PEO, as well as a band at ~2870 cm^{-1} due to the CH stretching vibration in the adsorbed PEO, whereas an absorption peak at 3675 cm^{-1} disappeared by fully covering the silanol groups with PEO molecules; (C) in a spectra of silica on which benzene is added at $\phi^d = 0.75$ after the full adsorption of PEO, an additional and weak band at ~3640 cm^{-1} due to the hydrogen bond between silanol group and benzene as well

Table I
Molar Volumes and Solubility Parameters of Solvent,[a] Displacers,[a] and PEO[b]

	V, cm^3/mol	δ, (cal/cm^3)$^{1/2}$		V, cm^3/mol	δ, (cal/cm^3)$^{1/2}$
CCl_4	97.0	8.6	methyl cellosolve	79.4	11.4
benzene	89.4	9.2			
dioxane	85.7	10.0	PEO		10.3
acetone	74.0	9.9			

[a] Reference 11. [b] Reference 12.

as the strong band at ~3050 cm^{-1} due to the CH stretching of adsorbed benzene appeared. It was found that the intensities of the bands at 3300 and 2870 cm^{-1} decrease whereas those at 3640 and 3050 cm^{-1} increase with an increase in ϕ^d of benzene. However, in the desorption of PEO by methyl cellosolve, acetone, and dioxane, since the band at 3300 cm^{-1} in the IR spectrum of the silica on which PEO is adsorbed resembles that of the silica on which the corresponding displacers are attached, we cannot investigate the desorption behavior of PEO by these displacers using the IR spectra of silica.

For evaluating a χ_s^{pd} value from eq 2, there are several unknown parameters in the equation besides for the ϕ_{cr}^d value. The lattice parameter $\lambda_1 = 0.25$, corresponding to a hexagonal lattice, is employed in the theoretical treatment of Cohen Stuart et al.[3] According to the suggestion of Cohen Stuart et al.,[3] the χ_{sc} value can be estimated from the displacement isotherm of a given polymer by a polymer repeating unit analogue. We should use the interaction parameters χ^{po}, χ^{pd}, and χ^{do}, which were determined thermodynamically or taken from references 7 and 8. Although the interaction parameters calculated from the solubility parameters may deviate from the true value, we daringly employ them in terms of the Hildebrand–Scatchard theory[9,10] as follow:

$$\chi = (V_{o(d)}/RT)(\delta_{o(d)} - \delta_{p(d)})^2 \qquad (3)$$

where V_o and V_d are the molar volumes of a solvent and a displacer, respectively, R is the gas constant, T is the absolute temperature, δ_o, δ_d, and δ_p are the solubility parameters of a solvent, a displacer, and a polymer, respectively. In calculation of χ values, we employed the molar volumes and solubility parameters listed in Table I.[11,12]

Since the chemical structure of dioxane resembles more the repeating unit of PEO than methyl cellosolve, we can assume $\chi_s^{pd} = 0$ for the displacement isotherm of PEO by the methyl cellosolve solvent, relying on the suggestion of Cohen Stuart et al.[3] For a calculation of a χ_{sc} value from eq 2, putting $\chi_s^{pd} = 0$, $\chi^{po} = 0.46$, $\chi^{pd} = 0.013$, $\chi^{do} = 0.31$, and $\phi_{cr}^d = 1.1_5$, $\chi_{sc} = -0.12$ is obtained. This calculated χ_{sc} value is negative and is not unreasonable since Cohen Stuart et al. also obtained the negative χ_{sc} value for the displacement of poly(vinylpyrrolidone).[3] This value is much smaller than the χ_{sc} value of 0.50 for PS in the same solvent[2] and this fact means that PEO chains can more easily adsorb on the silica surface in CCl_4 than PS chains.

Therefore, we can calculate a χ_s^{pd} value through eq 2 using the experimental values of ϕ_{cr}^d and χ_{sc} and also the interaction parameters, χ^{po}, χ^{pd}, and χ^{do}. The calculated χ_s^{pd} values are 0.58 for acetone and −1.2 for methyl cellosolve. These χ_s^{pd} values can be regarded as the adsorption energy parameter χ_s of PEO from acetone and methyl cellosolve. The χ_s^{pd} value for acetone is much larger than that for PS for the corresponding solvent.[2] Since the values of χ_s^{pd} for PS were negative, dioxane and acetone behaved as much stronger displacers for the desorption of PS than benzene. However, the order of the strength for the displacers among benzene, acetone, and dioxane is in good agreement for both polymers. In other words, the larger χ_s^{pd} values for PEO as compared with those for PS for the same displacer molecules correlates well with the preferential adsorption of PEO over PS for the competitive adsorption and displacement of both polymers, since the χ_s parameters are related to the adsorption strength.

In conclusion, the displacement of preadsorbed PEO at the silica surface by the addition of various displacers gives the adsorption free energy parameter of PEO from the corresponding displacer molecules by a simple route without data of the adsorbed amounts of the displacers. Then it is found that PEO molecules are more easily and tightly attached to the silica surface than PS from CCl_4, and this difference induces the preferential adsorption of PEO over PS.

Registry No. PEO, 25322-68-3; Aerosil 130, 7631-86-9; methyl cellosolve, 109-86-4; benzene, 71-43-2; acetone, 67-64-1; dioxane, 123-91-1.

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