Measurement of the Segmental Adsorption Energy of Poly(2-ethyl-2-oxazoline) on Silica in Water and Ethanol

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ABSTRACT: The segmental adsorption energy parameter, χ_s^{po}, was measured for poly(2-ethyl-2-oxazoline), PEOX, using a desorption/displacement technique. PEOX was desorbed from silica with five low molecular weight organic displacers in two solvents—water and ethanol—to obtain values of the critical volume fraction of the displacer at which the desorption was complete, ϕ_{cr}. The segmental adsorption energy for PEOX was 5.1 kT and 3.2 kT in water and ethanol, respectively. These values are consistent with the polymer adsorbing principally by hydrogen bonding between the carbonyl groups on the polymer and surface silanol groups. The difference in adsorption energies in water and ethanol reflects specific solvent effects that may be related to the negative excess entropy of mixing for water in PEOX solutions as well as due to the formation of hydrogen bond bridges between PEOX and silanol groups in water. The relatively high values of χ_s^{po} for PEOX in both solvents suggest that PEOX may serve as an effective anchor block in block copolymers adsorbing on surfaces by hydrogen bonding.

Introduction

The adsorption of nonionic, water-soluble polymers at an interface has significant scientific and technological importance. In recent years, considerable efforts have focused on understanding the factors controlling the structure of adsorbed homopolymer and copolymer layers on surfaces and how that structure affects interfacial behavior such as colloid stability, emulsification, wetting, and tribology.[1,2] Steric stabilization of concentrated colloidal suspensions, particularly with well-defined block copolymers, is important as a method for controlling the state of aggregation and hence the rheology and sedimentation behavior of concentrated ceramic slips, paints, and coatings.[3] Theoretical and experimental studies have focused recently on block copolymers[4-11] which can form self-assembled layers that hold great promise for tailoring interfacial properties. However, the development of water-soluble steric stabilizers has lagged behind that of polymer stabilizers soluble in organic solvents due to the complex structure of water and its interactions with polymers.

This work concerns a study of the adsorption of the nonionic polymer poly(2-ethyl-2-oxazoline), PEOX, on silica from water, ethanol, and binary mixtures. This polymer is especially interesting because it can be made with relatively narrow molecular weight distributions and because it can be incorporated in diblock copolymers with narrow molecular weight distributions. In recent work, Riffle *et al.* synthesized two new diblock systems—poly(dimethylsiloxane-2-ethyl-2-oxazoline)[12] and poly(ethyl vinyl ether-2-ethyl-2-oxazoline)—with relatively narrow molecular weight distributions.[13] These polymers are model systems for studying steric stabilization.

The solution properties of PEOX were described in an earlier paper.[14] PEOX homopolymer samples with relatively narrow molecular weight distributions were characterized by light scattering. At 25 °C, second virial coefficients gave values of the Flory polymer-solvent interaction parameter, χ^{po}, in water in the range 0.48-0.49 for M_w in the range 20-60 K while χ^{po} in ethanol lay in the range 0.32-0.35. A previous study had shown that the solubility of PEOX in water was due to the formation of hydrogen bonds with the carbonyl (C=O) group in the polymer chain,[15] while another study had shown that PEOX was soluble in a variety of polar organic solvents, particularly those capable of forming hydrogen bonds.[16] These solubility characteristics make PEOX particularly attractive since it is desirable to use copolymer stabilizers in solvents where micelles do not form since micelles can complicate copolymer adsorption and hinder stabilization.[4,5] At present, there is no block copolymer available in narrow molecular weight distributions in which both blocks are soluble in water.

The segmental adsorption energy parameter χ_s^{po} and the χ^{po} parameter describe the energetic aspects of polymer adsorption in the context of the mean field lattice theory developed by Scheutjens and Fleer.[17,19,20] The segmental adsorption energy, χ_s^{po} (kT), is defined as the change in free energy when a polymer segment adsorbs on a surface, thereby breaking contacts with solvent molecules and displacing solvent molecules from the surface.[17] In this paper, we report for the first time values of χ_s^{po} for PEOX on silica in water and ethanol. We follow the notation of Scheutjens *et al.* in which the superscript "p" denotes the polymer and the superscript "o" denotes the solvent in which the polymer is dissolved.[18] By definition, χ_s^{po} is positive if the polymer adsorbs preferentially from the solvent. The relatively high values of χ_s^{po} for PEOX in water and ethanol obtained in this work suggest the polymer has promise as an anchor block component in a block copolymer adsorbing onto surfaces such as metal oxides that possess hydrogen bonding groups.

The χ_s^{po} and χ^{po} parameters along with the degree of polymerization determine the mass of adsorbed polymer per unit area, Γ, and the structure of the adsorbed layer in terms of the fraction of segments in trains, tails, and loops, i.e. the segment distribution function. For a fixed value of molecular weight and χ^{po}, Γ and the fraction of segments adsorbed in flat trains increase with χ_s^{po}, up to $\chi_s^{po} \approx 2$, with a subsequent reduction in the fraction of segments adsorbed as loops or tails. This is important for polymeric dispersants since the interparticle potential is

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governed by the fraction of segments in tails.[20] For $\chi_s^{po} > 2$, Γ and the train fraction become essentially independent of χ_s^{po}.[31b]

The two principal methods for estimating the segment adsorption energy χ_s^{po} (kT) are microcalorimetry[21,22] and desorption by displacers.[18,23] Microcalorimetry is suitable for systems where the principal contribution to the free energy of adsorption is enthalpic since it does not measure entropic contributions to the free energy. However, when there is a large change of entropy of the solvent upon adsorption of the polymer chain, such as in aqueous solutions where water associates strongly with the polymer chain, microcalorimetry may not provide accurate measurements of χ_s^{po}.[18]

Cohen Stuart *et al.* have shown that a low molecular weight displacer with a sufficiently strong affinity for a surface may completely desorb a polymer chain at a critical displacer volume fraction ϕ_{cr} and that measurements of ϕ_{cr} for a series of displacers with various strengths permits a calculation of χ_s^{po}.[18,23] In addition to the importance of χ_s^{po} in the lattice theory for adsorption, the ability of a polymer to displace another polymer in a given solvent at a given degree of polymerization correlates with their relative values of χ_s^{po}. A polymer with a higher value of χ_s^{po} will displace a polymer with a lower value. This is important because many applications of polymeric dispersants occur in media where several soluble polymers are present in solution. For a diblock copolymer adsorbed at an interface, the solvated tail block is anchored to the surface by the anchor or head block. For efficient stabilizer performance, it is essential that χ_s^{po} for the anchor block be sufficiently larger than that for the tail block so that the tail is completely displaced.

There are relatively few studies of the adsorption energy for polymers with all but one of them focusing on polymers adsorbing onto metal oxides from relatively nonpolar organic solvents.[24-30] A series of papers by Cohen Stuart *et al.* on the adsorption of poly(vinylpyrrolidone), PVP, from water and dioxane is the only study to date on a water-soluble polymer in water.[23,31] This work is especially relevant to the present study of PEOX adsorption given the similarities of PEOX and PVP; i.e. both have an amide group with similar polarity, and the solution properties in water are similar—$\chi^{PEOX,w} = 0.48$–0.49 while $\chi^{PVP,w} = 0.47$. It was shown that PVP adsorbed on silica principally through hydrogen bonding of the carbonyl C=O on the polymer to silanol groups on the surface.[31,32] Low molecular weight organic displacers were used to desorb poly(vinylpyrrolidone), PVP, from silica in water and dioxane.[23] The experimental values of χ_s^{po}, ~4.0 in both water and dioxane, correlated well with the relatively high fraction of adsorbed segments in trains detected by NMR. These values will be compared in the Results and Discussion to the values of χ_s^{po} for PEOX measured in this study.

A recent study by van der Beek *et al.*[24-26] employed a variety of techniques including FTIR, thin-layer chromatography, microcalorimetry, and displacement processes to determine χ_s^{po} for a variety of polymers containing different functional groups adsorbing onto various metal oxides from various organic solvents. Values of χ_s^{po} ranging from 0.5 to 5.1 were measured depending on the polymer structure, solvent type, and substrate chemistry. All of these studies illustrate the complex relation between polymer adsorption and the structures of the polymer, solvent, and substrate. A deeper understanding of these interactions is essential for the systematic design of polymeric stabilizers.

This paper is organized as follows. The next section describes the theoretical basis for measuring χ_s^{po} developed by Cohen Stuart *et al.*[18] The experimental procedures used in the adsorption/displacement experiments are then described, followed by the discussion of results.

Theoretical Background

The displacement method is based on an approximate form of the mean field lattice theory of Scheutjens and Fleer which describes the conformations of polymer chains on and near the surface as sequences of segments in a lattice.[18,23] In the one-layer approximation, it is assumed that the adsorbed polymer segment density close to the point of complete desorption, i.e. $\phi = \phi_{cr}$, differs from the bulk solution concentration only in the lattice layer next to the surface. The χ_s^{po} parameter of the polymer adsorbing on the surface can be separated into two terms—the segmental adsorption energy parameter χ_s^{pd} of the polymer adsorbing from the pure displacer (d) and the χ_s^{do} parameter of the displacer adsorbing in the presence of solvent (o)

$$\chi_s^{po} = \chi_s^{pd} + \chi_s^{do} \tag{1}$$

The χ_s^{pd} parameter of the polymer adsorbing from pure displacer is related to the critical displacer volume fraction ϕ_{cr} by

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

where χ_{sc} (kT) is the minimum critical adsorption energy that a polymer segment must have to adsorb since the segment loses entropy upon adsorption, λ_1 is the lattice parameter (=0.25 for a hexagonal lattice), and $\Delta\chi^{do}$ is the solvency parameter, defined as

$$\Delta\chi^{do} = \chi^{pd} + \chi^{do} - \chi^{po} \tag{3}$$

where χ^{pd} and χ^{do} are the polymer–displacer and displacer–solvent interaction parameters, respectively. The critical volume fraction ϕ_{cr} is determined experimentally as the volume fraction of displacer which completely displaces the polymer from the surface. The χ_s^{do} parameter is obtained from the initial slope, S, of the displacer adsorption isotherm since this part of the isotherm contains information on the displacement of solvent molecules from active surface adsorption sites in the absence of displacer–displacer interactions. This part of the isotherm is also relatively insensitive to surface heterogeneities. The initial slope is defined as

$$S = \lim_{\phi_*^d \to 0} (\Gamma/\phi_*^d) \tag{4}$$

where Γ is the adsorbed amount of displacer in moles per unit area and ϕ_*^d is the volume fraction of displacer in the bulk solution. Cohen Stuart *et al.* showed that S is related to a dimensionless slope s by

$$s = \exp(\chi_s^{do} + \lambda_1\chi^{do}) \tag{5a}$$

$$= \Gamma_{mon}^{-1}(v_d/v_o)S \tag{5b}$$

where v_d and v_o are the molecular volumes of the displacer and solvent, respectively, and Γ_{mon} is the site density of isolated silanol groups on the silica surface. Substituting eqs 2 and 5 into eq 1 results in an equation relating χ_s^{po} to ϕ_{cr}:

$$\chi_s^{po} = \ln \phi_{cr} + \ln s + \chi_{sc} - \lambda_1 \chi^{po} + [(1 - \phi_{cr})(1 - \lambda_1) - \lambda_1]\Delta\chi^{do} \quad (6)$$

Adsorption will not occur if $\chi_s^{po} < \chi_{sc}$. The χ_{sc} parameter is obtained experimentally by measuring ϕ_{cr} for a displacer that is a low molecular weight analog of the polymer repeat unit. In this case, $\chi^{pd} = 0$ and $\chi^{po} = \chi^{do}$ so that $\Delta\chi^{do} = 0$ from eq 3. In addition, $\chi_s^{pd} = 0$ since the contact free energy of adsorption on the surface for both is approximately the same. Equation 2 then reduces to

$$\chi_{sc} = -\ln(\phi_{cr})_{\text{analog}} \quad (7)$$

If there is some solvency effect with the displacer, i.e. if χ^{pd} is not quite zero, then eq 7 is still a good approximation of eq 2 for relatively larger values of $(\phi_{cr})_{\text{analog}}$. The experimental values of χ_{sc} from eq 7 can be compared to the analytical result from the lattice model which accounts for the loss of conformational entropy of the polymer segment upon adsorption

$$\chi_{sc} = -\ln(1 - \lambda_1) \quad (8)$$

Values of χ_{sc} from eqs 7 and 8 will be compared in a later section.

An inspection of eq 6 shows that the calculation of the segmental adsorption energy χ_s^{po} requires values for the solvency parameter $\Delta\chi^{do}$ in addition to values of ϕ_{cr}, s, and χ^{po} which can be measured directly. Values of $\Delta\chi^{do}$ can be obtained by evaluating eq 2 for polymer displacement experiments for a given displacer "d" carried out from the solvents water (w) and ethanol (EtOH). Subtracting the two resulting equations gives

$$\ln(\phi_{cr}^{d,w}/\phi_{cr}^{d,EtOH}) + 0.75(1 - \phi_{cr}^{d,w})\Delta\chi^{d,w} - 0.75(1 - \phi_{cr}^{d,EtOH})\Delta\chi^{d,EtOH} = 0 \quad (9)$$

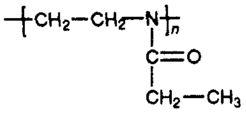
In a similar fashion, eq 6 can be evaluated for a common solvent "o" with two displacers d1 and d2:

$$\ln(\phi_{cr}^{d1,o}/\phi_{cr}^{d2,o}) + \ln(s^{d1,o}/s^{d2,o}) + (0.5 - 0.75\phi_{cr}^{d1,o})\Delta\chi^{d1,o} - (0.5 - 0.75\phi_{cr}^{d2,o})\Delta\chi^{d2,o} = 0 \quad (10)$$

For a given pair of displacers d1 and d2 and for the two solvents water and ethanol, eqs 9 and 10 generate four independent, linear, algebraic equations with the solvency parameters $\Delta\chi^{d,o}$ as the four unknowns. These are solved to obtain values of χ_s^{po} as discussed below.

Experimental Section

Materials. Samples of poly(2-ethyl-2-oxazoline), PEOX, were synthesized by cationic ring-opening polymerization using procedures described earlier by Riffle *et al.*[12] The structure of PEOX is given below:



Values of the weight-average molecular weight M_w for several samples, listed in Table 1 were measured by static light scattering and were reported in an earlier paper.[14] Values of the polydispersity index M_w/M_n, measured by gel permeation chromatography, were less than 1.3 for $M_n \leq 40$ K.[33] Cab-O-Sil EH-5 silica, manufactured by G. L. Cabot Inc., was used for the adsorption experiments. The surface area is 380 ± 30 m²/g.[34] The silica powder was dried by heating at 100–115 °C for typically 4 h and then stored in a desiccator prior to use. Pyridine (PYR), *N*-ethylacetamide (NET), dimethyl sulfoxide (DMSO), and furfuryl alcohol (FUR) were selected as the displacers because of their ability to act as proton acceptors. These displacers were expected to interact strongly with the acidic silanol (Si—OH) groups on the silica surface. The displacer chosen as a low molecular weight analog for PEOX was *N,N*-dimethylpropionacetamide, DMP, which is a precise analog of PEOX. DMP was obtained from Aldrich with a stated purity higher than 99.7%. All other displacers (HPLC grade) were purchased from Aldrich Chemical Co. and used as received. Deionized water and ethyl alcohol (Aaper Co., 200 Proof) were used as the solvents. Care was taken to avoid exposure of the displacers and ethanol to atmospheric moisture. The deionized water had a resistivity of 17×10^6 Ω cm and was obtained from a Barnstead NANOPURE II water purification system.

Table 1. Molecular Weight Characterization Data for Poly(2-ethyl-2-oxazolines)

sample	M_w[a]
PEOX 20K	23.1K
PEOX 30K	33.3K
PEOX 60K	65.4K

[a] Measured by static light scattering in water at 25 °C; M_w/M_n was approximately 1.19–1.54 as determined by gel permeation chromatography.[13]

Displacer Adsorption Isotherms. Adsorption isotherms for the four displacers on silica were measured in water and ethanol. The adsorption isotherms were determined by the conventional solution depletion method. Typically, an initial solution of approximately 2.5% (w/w) was prepared for each displacer in two solvents. Approximately 0.2 g of silica was mixed with 10 g of solution. The mixtures were gently rotated end-over-end for 24 h at ~25 °C. The suspensions were then centrifuged at 2250*g* for 10 min. The supernatants were carefully transferred to quartz cuvettes where the UV absorbance was measured with a Hitachi U-2000 UV/vis spectrophotometer at a low wavelength in the range 220–250 nm, according to different displacers, to determine the unadsorbed displacer concentrations. The amount of adsorbed displacer was then calculated through the comparison of the absorbance change. The measurement accuracy was ±2%.

Adsorption Isotherms of PEOX. Adsorption isotherms of PEOX on silica from water and ethanol were also determined by the solution depletion method very similar to that used for the displacer isotherms. The polymer concentration in the supernatant was measured at a wavelength of 238 nm. All experiments were carried out at ~25 °C. The measurement accuracy was ±2%.

Displacement Isotherms. Displacement isotherms were measured for the PEOX 30K (degree of polymerization DP ≈ 330) sample to determine the critical displacer volume fraction ϕ_{cr} in water and in ethanol for the four different displacers. Only one molecular weight was used since Cohen Stuart *et al.* demonstrated that the value of ϕ_{cr} was essentially independent of the molecular weight of the polymer for DP > 100.[18] The PEOX displacement measurements were performed with a modification of the solution depletion technique. Approximately 0.2 g of silica was mixed with 10 g of solutions of PEOX 30K dissolved in mixtures of a given solvent and displacer at various concentrations of displacer. The PEOX concentration was controlled at 1.6 g/L, well in the plateau regions of the individual PEOX adsorption isotherms. After equilibration for 24 h, the dispersions were centrifuged and the supernatants were withdrawn. Since the displacers and PEOX adsorbed at similar wavelengths, the residual displacers had to be first removed from the supernatant before measuring the concentration of PEOX. The solvents and displacers were first vaporized by heating at 100 °C in air followed by drying in a vacuum oven at 100 °C for 24 h. Deionized water was then added to the dry polymer and the entire heating cycle was repeated at least twice. In the final step, deionized water was added to the dry polymer and the polymer concentration was measured spectrophotometrically.

Thin Layer Chromatography. Thin layer chromatography (TLC) was performed to provide an independent measurement of ϕ_{cr} for pyridine in water. TLC has been shown to be a very sensitive method for determining ϕ^{cr}.[26] Whatman K5F silica gel

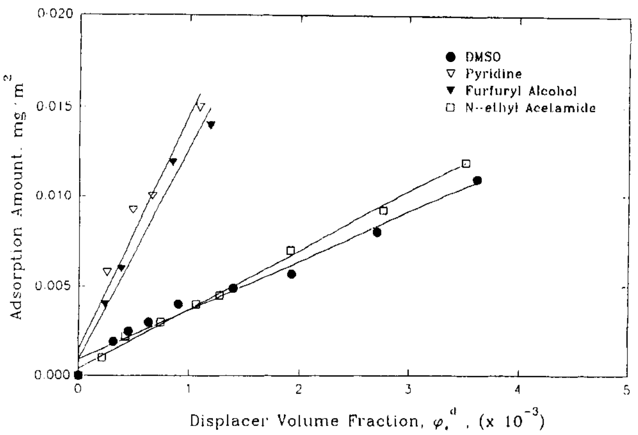


Figure 1. Adsorbed amount of displacers, mg m^{-2}, as a function of displacer volume fraction $\phi_*{}^d$ from water onto Cab-O-Sil EH-5 silica: (●) dimethyl sulfoxide; (▽) pyridine; (▼) furfuryl alcohol; (□) *N*-ethylacetamide.

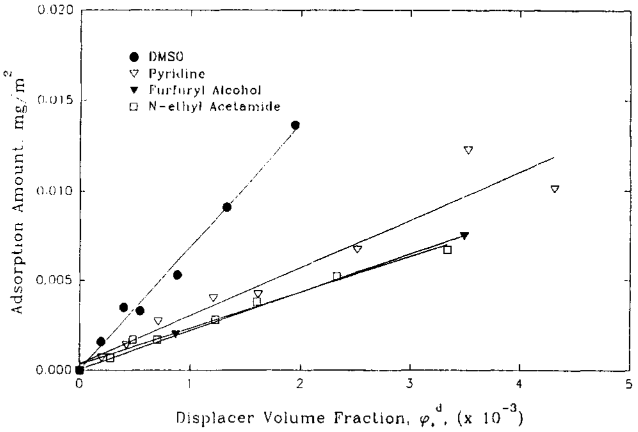


Figure 2. Adsorbed amount of displacers, mg m^{-2}, as a function of displacer volume fraction $\phi_*{}^d$ from ethanol onto Cab-O-Sil EH-5 silica. Symbols are the same as in Figure 1.

TLC plates, purchased from Alltech Associates Inc. (Deerfield, IL), with a silica layer of 0.25 mm were used for the thin-layer chromatographic experiments. The plates were dried in air at 120 °C for 12 h prior to use. Spots of PEOX were deposited along a start line with 2 cm from the lower edge of the plate. The plate was then placed above the eluent of the appropriate composition in a closed glass development tank for 45 min in order to establish equilibrium between the vapor phase, the liquid phase, and the adsorbed phase on the silica. The upward elution was started by lowering the plate just into the eluent. After elution the plates were dried, then sprayed with a 2% iodine aqueous solution and dried again. A dark spot would appear, indicating the position of PEOX on the plate, from which the R_f values, defined as the ratio of the distance from the polymer spot to the start line to that from the liquid front to the start line, were measured.

Results and Discussion

Displacer Isotherm. The displacer adsorption isotherms in water, Figure 1, and in ethanol, Figure 2, were measured at sufficiently low displacer concentrations to obtain values of the slope "S" in the initially linear part of the isotherm. The slopes were determined by least squares regression. These slopes are relatively insensitive to surface heterogeneities and to interactions between adsorbed displacer molecules. From eq 5b, the scaled slope "s" was calculated using a value of the site density of active silanol groups cited by Kiselev for silica heated to 700 °C, $\Gamma_{\text{mon}} = 2.33 \times 10^{-6}$ mol m^{-2}.[35] This value was recommended by Cohen Stuart *et al* on the basis of a previous study of the adsorption of the related polymer PVP on silica which showed that only isolated silanols that persist upon heating to elevated temperatures were the active sites for hydrogen bonding with PVP.[23] Values of the dimensional slope "S" and the natural log of the scaled slope "s" are listed in Table 2. Relative standard deviations of S were typically 5–10%. This led to less than ±2% variation in the calculated values of $\chi_s{}^{\text{po}}$.

Table 2. Initial Slopes of Displacer Adsorption Isotherms on Silica

	initial slope, 10^5S, mol m^{-2}		ln s^a	
displacers	water	ethanol	water	ethanol
DMSO (dimethyl sulfoxide)	3.46	8.72	4.07	3.82
PYR (pyridine)	11.8	3.41	5.43	3.02
NET (*N*-ethylacetamide)	3.79	2.30	4.44	2.77
FUR (furfuryl alcohol)	12.0	2.14	5.51	2.61

[a] s obtained from eq 5b where $\Gamma_{\text{mon}} = 2.33 \times 10^{-6}$ mol m^{-2}.

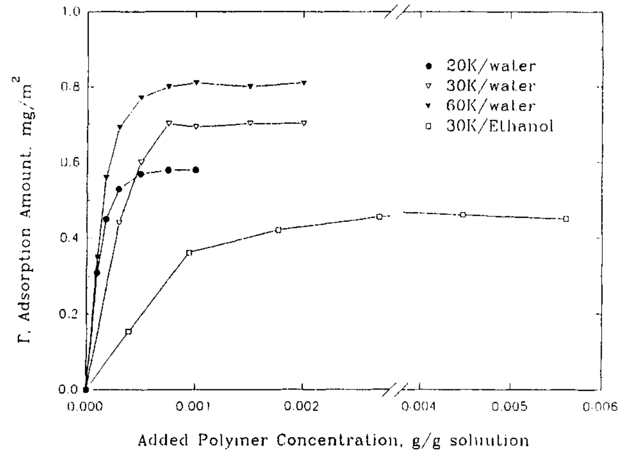


Figure 3. Adsorbed amount of PEOX, mg m^{-2}, as a function of concentration of added PEOX concentration, g of PEOX/g of solution. Three different molecular weights (defined in Table 1) are shown in different solvents: (●) 20K/water; (▽) 30K/water; (▼) 60K/water; (□) 30K/ethanol.

Cohen Stuart *et al.*[23] also measured values of S_{PYR} and S_{DMSO} for Cab-O-Sil M5 in water which are somewhat lower than our corresponding values—$S_{\text{PYR}} = 5.3 \times 10^{-5}$ mol m^{-2} as compared to our value of 11.8×10^{-5} mol m^{-2} and $S_{\text{DMSO}} = 2.8 \times 10^{-5}$ mol m^{-2} as compared to our value of 3.46×10^{-5} mol m^{-2}. The differences may be due to the range of displacer volume fraction used in our study, $0 \le \phi_*{}^d \le 0.005$, whereas the slopes reported by Cohen Stuart *et al.* appear to have been calculated over the range $0 \le \phi_*{}^d \le 0.01$. Some curvature in the isotherm in that range may have led to somewhat lower slopes. The slopes in Table 2 were always calculated with a minimum of four data points and usually with as many as six to eight points. The differences in S are not due to the different types of silica used since EH-5 and M-5 have similar surface silanol densities.[34] Given the limited comparison of slopes available, it is difficult to assess the effect that these differences may have on the comparison of our values of $\chi_s{}^{\text{po}}$ for PEOX and those for PVP.

PEOX Adsorption Isotherm. Figure 3 depicts the adsorption isotherms of PEOX samples on the silica surface from water for three molecular weights and from ethanol for PEOX 30K. The adsorption isotherms rose steeply with increasing polymer concentration, especially for PEOX 20K and 60K, and all reached a plateau, indicating saturation of the surface. The adsorption isotherms are of the high-affinity type which is characteristic for high polymers. The plateau adsorption amounts of PEOX in water increased steadily with molecular weight, ranging from 0.57 to 0.80 mg m^{-2}. The plateau adsorption

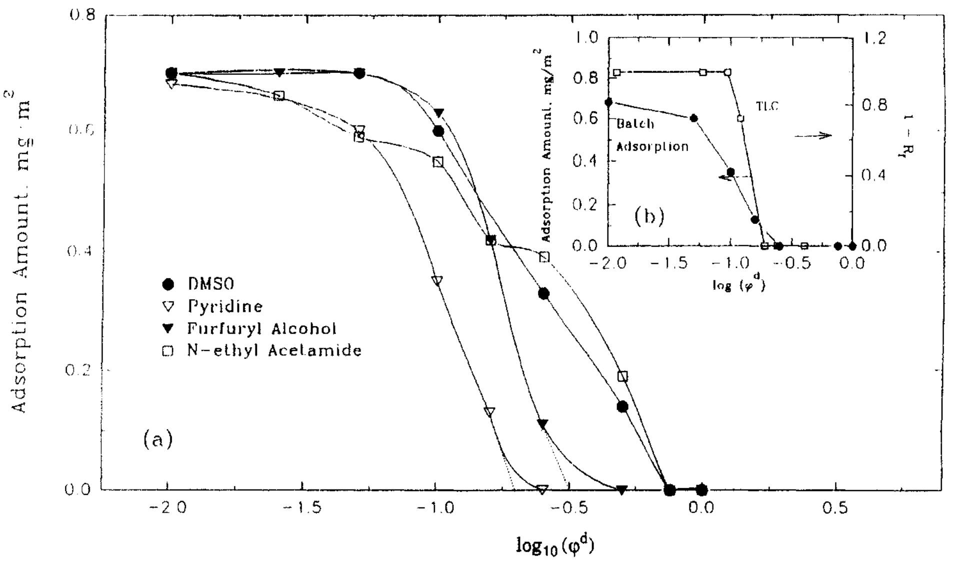


Figure 4. (a) Displacement isotherms of PEOX from silica for the displacers. The symbols are the same as in Figure 1. (▲) *N,N*-dimethylpropionamide. The values of ϕ_{cr} are obtained from the interpolation of each curve to zero adsorbed amount. (b) Adsorbed amount of PEOX, mg m^{-2}, as a function of retention determined by thin layer chromatography, expressed as $(1 - R_f)$ for PEOX in the solvent mixture water–pyridine and batch desorption process as a function of the volume fraction ϕ_*^d of pyridine. (□) TLC method; (●) displacement method.

Table 3. Critical Displacer Volume Fractions for PEOX 30K

solvent	displacer^a	$\ln(\phi_{cr})$	ϕ_{cr}
water	PYR	-1.54	0.21
	PYR (TLC)^b	-1.56	0.21
	FUR	-1.0	0.37
	NET	-0.46	0.63
	DMSO	-0.28	0.76
	DMP (*N,N*-dimethyl-propionacetamide)	-0.99	0.37
ethanol	PYR	-0.69	0.50
	FUR	-0.30	0.74
	NET	-0.58	0.56
	DMSO	-1.15	0.32
	DMP	-0.78	0.46

[a] Abbreviations are the same as in Table 2. [b] Determined by thin layer chromatography (TLC).

amount of PEOX 30K in ethanol, 0.46 mg m^{-2}, was significantly less than the corresponding value in water, 0.70 mg m^{-2}. This is related to the greater solubility of PEOX in ethanol, i.e. $\chi^{po} = 0.32$ in ethanol compared to $\chi^{po} = 0.48$ in water.[14]

Displacement Isotherms for PEOX. The displacement isotherms in Figure 4 for PEOX 30K in water show that all four displacers were capable of completely displacing PEOX. The adsorbed mass of PEOX per unit area Γ, decreased with increasing volume fraction of displacer in equilibrium with the silica, ϕ_*^d, reaching zero at the critical displacer concentration ϕ_{cr}. Similar displacement curves were found for PEOX 30K in ethanol. In those instances where the displacement curve did not drop abruptly to zero, ϕ_{cr} was obtained by interpolation, as illustrated for pyridine and furfuryl alcohol in Figure 4a. Excellent agreement was found between the interpolated value for pyridine in water and the value obtained by thin layer chromatography as shown in Figure 4b.

Two significant features of the displacement isotherms were their shapes and the relative orders of ϕ_{cr} for the displacers in ethanol and water, summarized in Table 3. The curves in water and ethanol do not exhibit minima, indicating relatively strong displacer effects. The order of ϕ_{cr}, i.e. the relative strengths of the displacers, was not the same in water and in ethanol. The displacer strength in water as given by the order of ϕ_{cr} increased in the order DMSO < NET < FUR < PYR. In ethanol, the displacer strength increased in the order FUR < NET < PYR < DMSO. This suggests the importance of nonzero values of the solvency parameter $\Delta\chi^{do}$ since for athermal solutions, i.e. $\Delta\chi^{do} = 0$, the order of displacer strength is independent of solvent type.

Critical Displacer Energy. The critical adsorption energy parameter, χ_{sc}, can be estimated from the lattice model using eq 8 and can be estimated from eq 7 with desorption experiments where the displacer is chosen to match the repeat unit of the polymer so that $\chi_s^{pd} = 0$ and $\Delta\chi^{do} = 0$. For a hexagonal lattice with the lattice parameter $\lambda_1 = 0.25$, $\chi_{sc} = 0.288$. Equation 7 is valid when χ_s^{po} is not too small, i.e. $\chi_s^{po} > 2$,[27] which is satisfied in this study. Given the values of $(\phi_{cr})_{NET}$ listed in Table 3, $\chi_{sc} = 0.99$ in water and 0.78 in ethanol. These are somewhat higher than the theoretical value of 0.288, most likely because the lattice theory assumes no specific interactions between the polymer, solvent, and surface. This is not the case with the present system where hydrogen bonding is important. Additional effects of specific interactions will be seen below in the calculations of the solvency parameter $\Delta\chi^{do}$. The experimental values of χ_{sc} were used to obtain self-consistent calculations of χ_s^{po}.

Calculation of χ_s^{po}. The solvency parameters $\Delta\chi^{do}$ were calculated from eqs 9 and 10 for various combinations of the two solvents and four displacers. This was done with the values of ln *s* and ϕ_{cr} listed in Tables 2 and 3, respectively, along with the values of χ^{po} for PEOX at 25 °C noted earlier—$\chi^{po} = 0.48$ in water and $\chi^{po} = 0.32$ in ethanol. Values of χ_s^{po} were then calculated from eq 6 and are summarized along with values of $\Delta\chi^{do}$ in Table 4. To test the self-consistency of the data, calculations were made for the three different combinations of displacers resulting in six independent values of χ_s^{po} and three independent values of $\Delta\chi^{do}$ in a given solvent. These values should be independent of the particular pair of displacers used. The values of χ_s^{po} were quite self-consistent, with an average value of 5.1 in water and 3.2 in ethanol. The relative standard deviations of the averages for χ_s^{po} were 4% and 9% for water and ethanol, respectively. There was considerably more scatter in the values of $\Delta\chi^{do}$ due to an accumulation of experimental errors and to effects neglected by the lattice model such as specific association

Table 4. Segmental Adsorption Energy, χ_s^{po}, and Combined Solvency Parameter, $\Delta\chi^{do}$, for Poly(2-ethyl-2-oxazoline) on Silica for Various Combinations of Solvents and Displacers

	$\Delta\chi^{do}$		χ_s^{po}	
	water	ethanol	water	ethanol
PYR	2.13	1.07	5.5	3.1
FUR	0.41	−2.59		
DMSO	−5.29	−1.94	5.0	3.3
NET	5.93	5.34		
DMSO	−3.02	0.63	4.9	3.5
FUR	−2.34	−9.03		
PYR	0.11	−2.10	4.9	2.7
NET	−2.30	−1.57		
PYR	1.40	−0.08	5.2	3.0
DMSO	−8.52	−1.35		
FUR	−1.48	−7.22	5.1	3.4
NET	7.38	6.55		
			5.1 ± 0.2[a] (av)	3.2 ± 0.3[a] (av)

[a] Standard deviation of the average value of χ_s^{po}.

of water molecules with the PEOX chain. Given this latter point, the experimental values of $\Delta\chi^{do}$ cannot be interpreted strictly in terms of the regular solution theory. However, it is noted that the term in eq 6 that contains $\Delta\chi^{do}$ was typically ≤15% of the calculated value of χ_s^{po} for a given combination of displacers in a given solvent. Only for the displacer combination of furfuryl alcohol/dimethyl sulfoxide in ethanol did the term containing $\Delta\chi^{do}$ reach 34% of the value of χ_s^{po}. There is no significant change in the average value of χ_s^{po} in ethanol if this set of displacers is ignored.

The higher adsorption energy of $\chi_s^{p,\mathrm{water}}$ is due to solvent effects. Earlier studies have shown that the excess entropy of mixing, Δs^E, of water in PEOX solutions was negative due to specific association between water and the polymer, i.e. by hydrogen bonding.[14,15] The adsorption of segments in trains may partially disrupt hydrogen bonding between water and those segments, leading to a decrease in specific association of water with the chains and thus an increase in the entropy of water molecules. Thus, the adsorption of segments in trains would be favored by the increase of entropy of the water.

Another possible solvent effect is the participation of water in forming hydrogen bond bridges between the polymer and surface silanol groups since a water molecule can form two hydrogen bonds at once. This bridging would be in addition to direct hydrogen bond formation between the carbonyl oxygen on PEOX and surface hydroxyl groups. In ethanol, only direct hydrogen bonding is possible since ethanol itself can only form one hydrogen bond at a time. This bridging might circumvent steric hindrances to direct hydrogen bond formation between a given carbonyl group and silanol group.

By comparison, Cohen Stuart *et al.* measured χ_s^{po} for PVP adsorbed onto silica from water and dioxane to be approximately 4 kT using the displacement technique.[23] This agreed quite well with the value obtained by microcalorimetry where the monomer analog *N*-ethylpyrrolidone was adsorbed on silica from both water and dioxane.[31b] Solvent entropic effects were presumed to be negligible since both methods agreed well.

The higher value of the plateau adsorption amount of PEOX 30K in water, 0.70 mg m^{-2} compared to 0.46 mg m^{-2} in ethanol is a consequence of the lower solubility of the polymer in water. The differences in the segmental adsorption energy parameters in water and ethanol are probably not important here since both values are higher than 2. In this range, the plateau adsorption amount Γ_p is relatively insensitive to further increases in χ_s^{po}.

The difference of 1.1 kT between our average value for PEOX in water and Cohen Stuart's value for PVP in water may be accounted for given the differences in the structures of the two polymers, the approximations in the lattice theory, and possibly the differences in displacer isotherm slopes noted earlier. Van der Beek reported significant differences in values χ_s^{po} for polymers with closely related structures. For example, the adsorption energy of poly(ethylene oxide), PEO, $[-(CH_2)_2-O-]_x$, on silica from carbon tetrachloride, 5.1 kT, exceeded that of poly(tetrahydrofuran), PTHF, $[-(CH_2)_4-O-]_x$, by 1.2 kT.[25] The adsorption energy of poly(methyl methacrylate), PMMA, 4.3 kT, exceeded that of the more bulky poly(butyl methacrylate), PBMA, by ~1.4 kT also on silica from carbon tetrachloride. These two polymers have carbonyl groups in side groups. For polymers adsorbing onto silica from organic solvents, it was generally found that χ_s^{po} decreased with an increase in the number of methylene groups in the main chains or with the increasing size of alkyl side groups.[24]

Finally, it is noted that the magnitudes of the χ_s^{po} values for PEOX in water and ethanol are relatively high compared to those for polymers that interact with surfaces by means other than hydrogen bonding. For example, van der Beek *et al.* measured values of $\chi_s^{po} = 1.0$ and 1.9 for polystyrene (PS) adsorbing onto silica from carbon tetrachloride and cyclohexane, respectively.[26]

Conclusions

The adsorption of poly(2-ethyl-2-oxazoline), PEOX, was studied using the displacement technique developed by Cohen Stuart *et al.* The addition of various low molecular weight displacer molecules from two different solvents—water and ethanol—gave values of the critical displacer volume fraction ϕ_{cr}. The average values of the segmental adsorption energy parameter χ_s^{po} were 5.1 and 3.2 in water and ethanol, respectively. These relatively high values are attributed to hydrogen bonding between carbonyl groups on the polymer and surface silanol groups. The difference in adsorption energies in water and ethanol reflects specific solvent effects that may be related to the negative excess entropy of dilution for water in PEOX solutions as well as due to the formation of hydrogen bond bridges between PEOX and silanol groups in water. The relatively large magnitude of χ_s^{po} for PEOX in water and ethanol suggests that PEOX may serve as an effective anchor block in block copolymeric stabilizers.

The solvent effects point to the need for further work to separate the effect of solvent enthalpic and entropic effects in polymer adsorption. Microcalorimetry experiments can measure the enthalpy of adsorption of DMP on silica from water and ethanol which will be compared with the values of χ_s^{po}. Machine simulation of solvent–segment interactions should also prove useful in gaining a qualitative understand of the role polymer structure plays in structuring solvent molecules, particularly water, around chain segments.

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