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The Collapse of Poly(ethylene oxide) Monolayers

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ABSTRACT: Surface pressure π has been measured as a function of surface concentration for poly(ethylene oxide) (PEO) surface films, spread onto deionized water at temperatures T from 8 to 28 °C. At fixed surface coverage, the temperature coefficient of surface pressure $d\pi/dT$ was negative at submonolayer coverages and positive at higher surface coverages. This suggests, respectively, a peculiar increase and decrease of surface entropy with increasing surface coverage. The equilibrium spreading pressure from an excess of polymer, π_{eq}, was achieved at surface coverage 0.8 mg/m^2, approximately 1.5 times monolayer coverage. As a function of molecular weight, π_{eq} was constant beyond molecular weight $M \approx 1 \times 10^5$ g/mol but fell at lesser levels for fractions of lesser molecular weight. Observation of $d\pi/dT < 0$ appears to have been observed previously only for the spreading of small crystalline amphiphiles, but the reasons cannot be the same in the present system. A degree of ordering of water molecules with the PEO repeat unit in the surface layer is suggested. These findings illustrate that a polymer monolayer should not in all respects be considered as two-dimensional.

Introduction

The nature of monomolecular films is poorly understood. The issue is pursued in several areas of study: gases adsorbed onto solids under conditions of high vacuum,[1] self-assembled monolayers of amphiphilic surfactants adsorbed onto solids by a Langmuir–Blodgett deposition process[2] or from liquid solution,[3] and classical amphiphilic surfactants[4] or polymers[5–10] spread as insoluble monolayers onto liquid surfaces. Much of the above work has proceeded fairly independently, but common themes prevail: among them, the extent to which the monolayers are strictly two-dimensional and the search for an equation of state. Two-dimensionality is sometimes assumed,[6–8] but the phenomenon can also be viewed as predicated on the existence of very strong substrate–adsorbate interactions, combined with adsorbate–adsorbate interactions, a situation which may lead even at sub-monolayer coverage to quasi-two-dimensional structures.[11,12] This raises the interesting general question of passage to the three-dimensional state as the adsorbate concentration is raised to a level too high to be accommodated in a single layer.

Few homopolymers form monomolecular films at the water–air interface.[5] Relatively nonpolar species, such as polybutadiene, ball up instead into a lens; many polyelectrolytes, such as poly(styrenesulfonate), dissolve (though they may adsorb when the solution concentration is finite). Homopolymers that do spread contain amphiphilic character in each repeat unit. Examples studied in recent years are poly(vinyl acetate),[6] poly(methyl methacrylate),[6] poly(methyl acrylate),[7] poly(dimethylsiloxane),[9,10] poly(tetrahydrofuran),[8] and poly(ethylene oxide).[8] In these studies, behavior at surface coverages too low to constitute a complete monolayer has been emphasized.

The poly(ethylene oxide) (PEO) molecule is so surface-active that it forms an insoluble monolayer despite being water-soluble, at moderate temperature, in all proportions.[13] For a polyether to be water-soluble is unusual and much study of the solution properties of PEO has ensued.[13,26] Direct study of the monolayer is difficult owing to its low mass, less than 1 mg/m^2, but thermodynamic measurements of surface tension can be made relatively easily. With a Langmuir trough filled with water, it is possible to spread material to a known surface concentration, Γ, and to measure the associated surface pressure, π, the amount by which the liquid's surface tension is depressed by presence of the surface film.

In a previous study of PEO monolayers, Kawaguchi and co-workers[8] concluded from the dependence of π on surface concentration that scaling laws describing a strictly two-dimensional film held up to a concentration of ca. 0.3 mg/m^2. Shuler and Zisman[14] concluded from hysteresis in pressure-concentration isotherms that collapse of PEO into the aqueous substrate occurred upon compression to concentrations above 0.4 mg/m^2 (specific area 18 Å^2/segment); in addition to surface pressure, they measured the wave-damping coefficient and the surface potential. Glass[15] had earlier studied the surface tension of dilute PEO solution, finding π to be in the same range as in the monolayer work. Cohen-Stuart and co-workers,[16] in provocative experiments on a family of water-soluble polymers including PEO, observed for adsorbed layers a yield stress using a sensitive surface viscometer. Sauer and co-workers[17] have studied monolayers of a PEO–polystyrene diblock copolymer.

In the present work, we report the influence of temperature on the pressure–concentration equation of state, allowing us to separate the enthalpic and entropic contributions to the surface pressure. We address PEO at submonolayer coverages and also at coverages too high to sustain a single layer.

Experimental Section

Poly(ethylene oxide) standards (Toyo-Soda Ltd.) were purchased with weight-average molecular weights M_w = 1.8 × 10^4, 3.9 × 10^4, 8.6 × 10^4, 1.4 × 10^5, 2.5 × 10^5, and 5.9 × 10^5 g/mol and ratios M_w/M_n (M_n the number-average molecular weight) less than 1.10. An additional sample of low molecular weight (Polysciences Grade 4000) was stated to have M = 3000–3700. Most of the data reported below concerns the PEO species with M_w = 2.5 × 10^5 (M_w/M_n = 1.04). We denote this species as polymer A.

A sample of fractionated poly(vinyl acetate), M_n = 411 000, was generously donated by Professor John D. Ferry.

Experiments were performed inside a Teflon trough mounted within a thermostated chamber. The Wilhelmy plate method was used to measure surface pressure. A sand-blasted platinum foil 2 cm long was flamed and then suspended with one end in the water and the other end hanging from a Sartorius 1712 balance. Spreading solutions were prepared by weight in distilled chloroform or benzene (findings were the same with use of either spreading solvent), and π was inferred from lessened vertical force per length after the films were spread. Surface concentration was controlled by adding spreading solution from a micrometer-driven pipette at fixed surface area. This has advantages, in regard to making equilibrium measurements when the surface coverage is high, over the conventional compression method.[18] The resolution in π was 0.01 mN/m.

To measure the equilibrium spreading pressure,[4] a fragment of undiluted polymer (ca. 100 μg, i.e., a large excess) was dropped onto the water. This proceeded to dart about on the surface from surface pressure gradients for about 1 min, and after 15 min the surface pressure appeared to have equilibrated. At this time, the

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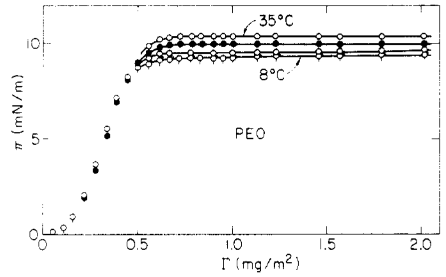

Figure 1. Surface pressure plotted against surface concentration for polymer A: (○) 35 °C; (●) 28 °C; (Q) 18.5 °C; (ϙ) 8 °C.

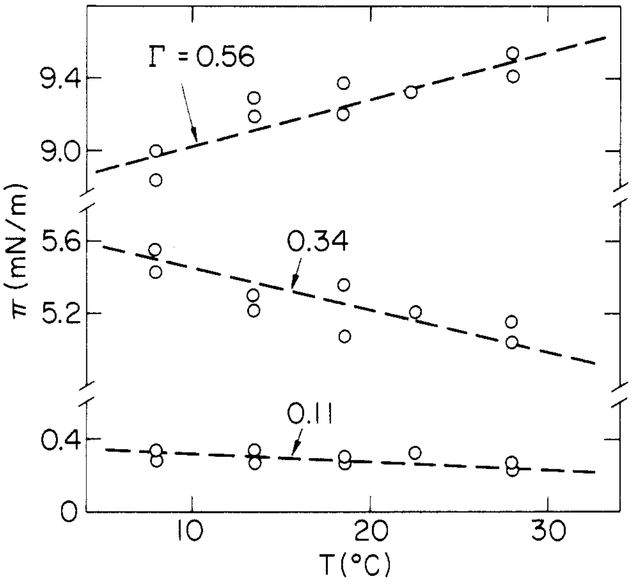

Figure 2. Surface pressure at constant surface concentration plotted against temperature, at three surface concentrations as indicated, for polymer A. Units of surface concentration are mg/m^2.

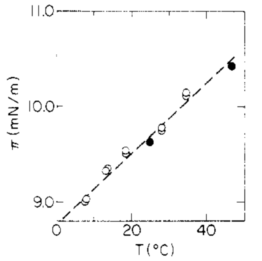

Figure 3. Surface pressures plotted against temperature, for polymer A: (○) Γ = 1.01 mg/m^2; (●) equilibrium spreading pressure.

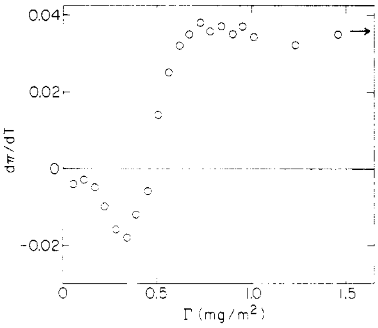

Figure 4. Linear temperature coefficient of surface pressure plotted against surface concentration, for polymer A.

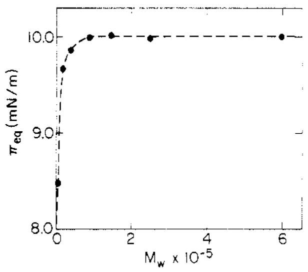

Figure 5. Equilibrium spreading pressures of PEO plotted against molecular weight.

undiluted polymer was no longer visible and appeared to have dissolved in the aqueous phase.

Results

Polymer A. Figure 1 shows pressure–concentration isotherms for polymer A (M_w = 250 000) at several temperatures from 8 to 35 °C. More data were taken than are plotted. The isotherm spans three qualitative zones of behavior. In the dilute zone of low surface concentration, π depends[5-8] on the density of molecules and hence on the molecular weight; for polymer A, $\pi = 0$ within experimental resolution in this zone. There follows a so-called semidilute[6-8] or transition[9] zone, where π rises rapidly and follow a power law in Γ; we have confirmed the power of 2.85 first reported[8] by Kawaguchi and co-workers. At $\Gamma \approx 0.30$ mg/m^2 there is a point of inflection, and beyond $\Gamma \approx 0.8$ mg/m^2 π is constant within experimental uncertainty. These features prevailed at every temperature, but the quantitative levels of $\pi(\Gamma)$ depended on temperature.

In Figure 2, surface pressure at fixed surface concentration is plotted against temperature at three levels of moderate surface coverage. There is a clear transition from slope $\mathrm{d}\pi/\mathrm{d}T < 0$ (Γ = 0.34 mg/m^2) to $\mathrm{d}\pi/\mathrm{d}T > 0$ (Γ = 0.56 mg/m^2). However, $\mathrm{d}\pi/\mathrm{d}T$ in the plateau zone is sensibly constant. This is illustrated in Figure 3, where π (1.01 mg/m^2) and the equilibrium spreading pressure, π_{eq}, appear to fall on the same curve with positive slope.

The curves appear to be linear within the limits of experimental error. Accordingly, slopes $\mathrm{d}\pi(\Gamma)/\mathrm{d}T$ were calculated by linear regression. These are plotted for many surface concentrations Γ in Figure 4. At low concentrations the data grow increasingly negative with increasing concentration. It is possible that they lie on a straight line, so that $\mathrm{d}\pi(\Gamma)/\Gamma\mathrm{d}T$ would be constant, but the data are too scattered to decide. The data then change sign over a range of concentrations and finally reach a positive level equal to the temperature coefficient of the equilibrium spreading pressure (denoted in Figure 4 by an arrow).

Effect of Molecular Weight. A positive temperature coefficient of surface pressure in the plateau zone was verified for the other PEO species. However, the level of the plateau depended on the molecular weight unless this was sufficiently high. As shown in Figure 5, the equilibrium spreading pressure was constant beyond M $\approx 1 \times 10^5$ but fell at lesser levels for fractions of lesser molecular weight. Such an effect for insoluble monolayers appears to be peculiar to PEO. It may be associated with the effect of polymer molecular weight on thickness of the surface film.

Comparison with Poly(vinyl acetate). The variations with temperature reported above also appear to be peculiar to PEO. However, since other data in the literature (see below) refer to polymers with sharper transition zones, corresponding to "poor surface solvent" in the scaling[6-8] ansatz, comparison was made with another polymer that exhibits the same power law in the transition zone. Poly(vinyl acetate) (PVAc) obeys $\pi \sim \Gamma^{2.85}$ in the transition zone, corresponding to a "good surface solvent".[6]

In Figure 6, surface pressure is plotted versus surface concentration at two temperatures for PVAc. Data at

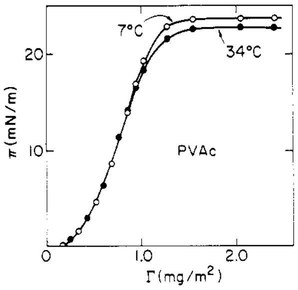

Figure 6. Surface pressure plotted against surface concentration for poly(vinyl acetate) at two temperatures as indicated.

other temperatures (not shown) were taken to confirm the results. In the plateau zone, the temperature coefficient of the surface pressure is negative. Furthermore, within the experimental uncertainty (±0.005 mN/(m·deg) in this case), $d\pi/dT = 0$ in the power law region. The behavior of PVAc thus differs from that of PEO.

Discussion

Entropy and Enthalpy Relations. As pointed out long ago by Crisp,[5] the temperature coefficient of the surface pressure is proportional to the differential surface entropy. Let G be the Gibbs free energy, H the enthalpy, S the entropy, A the area per polymer segment, N_2 the number of adsorbed molecules, and T the absolute temperature. By differentiating G with respect to A, at constant temperature and pressure, we obtain

$$\pi = -\left(\frac{\delta G}{\delta A}\right)_{N_2} = -\left(\frac{\delta H}{\delta A}\right)_{N_2} + T\left(\frac{\delta S}{\delta A}\right)_{N_2} \qquad (1)$$

Over a narrow temperature range, it is reasonable to consider the partial derivatives on the right side of eq 1 to be independent of temperature, so that

$$s^s \equiv \left(\frac{\delta S}{dA}\right)_{N_2} \approx \left(\frac{\delta \pi}{\delta T}\right)_{N_2} \qquad (2)$$

and

$$h^s \equiv \left(\frac{\delta H}{\delta A}\right)_{N_2} \approx T\left(\frac{\delta \pi}{\delta T}\right)_{N_2} - \pi \qquad (3)$$

In the above equations, the area per segment is inversely proportional to the experimental variable, surface concentration. Let A have the units Å^2/segment and Γ the units mg/m^2, and let N_A be Avogadro's number and M_0 the molar mass of a polymer segment. Then

$$A = 10^{23} M_0 / N_A \Gamma \qquad (4)$$

A positive temperature coefficient of surface pressure thus implies that entropy decreases with increasing surface concentration, and vice versa.

The relevant data are plotted in Figure 4. We conclude that at surface coverages below 0.5 mg/m^2, entropy rises with increasing surface coverage; that at still higher surface coverage, entropy is lost with increasing surface coverage; and that above 0.7 mg/m^2 the differential loss reaches a constant level, ca. −0.035 mJ/(m^2·deg). As discussed further below, the change in sign of s^s appears to occur around monolayer coverage.

As illustrated in Table I, the differential enthalpy calculated from eq 3 generally parallels in sign the differential entropy. The quantity h^s is slightly endothermic at high surface coverage; i.e., the differential change in heat is slightly exothermic with increasing surface concentration. This may be compared with the differential heat of dilution of PEO in solution, which appears to be exothermic.[26]

Table I
Differential Entropy and Enthalpy Values for Polymer A at the Air–Water Interface

Γ (mg/m^2)	s^s (mJ/(m^2·deg))	h^s (mJ/m^2)[a]
0.11	−0.003	−1.1
0.22	−0.010	−4.8
0.33	−0.018	−10
0.45	−0.006	−10
0.56	0.025	−1.8
0.67	0.035	0.9
0.78	0.036	0.9
0.95	0.037	1.1
∞[b]	0.037	1.0

[a] Evaluated at 28 °C. [b] Evaluated from π_{eq}.

Zones of constant surface pressure, interpreted as representing phase equilibria, are commonly analyzed by the Clausius–Clapeyron equation in two dimensions[21,22]

$$\left(\frac{\delta \pi}{\delta T}\right)_{N_2} = \frac{\Delta H}{T A_t} \qquad (5)$$

Here ΔH is the enthalpy difference between the two phases and A_t the specific area at the transition. For small amphiphiles in equilibrium with an excess of insoluble crystalline amphiphile, ΔH calculated from eq 5 is consistent with the known enthalpy of fusion.[23] Equation 5 has also been applied to the plateau zone of poly(n-alkyl methacrylates), i.e., to the hypothetical equilibrium in this instance between the two-dimensional film and the collapsed, noncrystalline, three-dimensional film.[21] It is interesting to make the same calculation for PEO. Although the numerical value of A_t is not sharply defined, choosing A_t = 5 Å^2/segment (Γ = 0.7 mg/m^2), one finds $\Delta H \approx 8$ kT/segment. Unfortunately, this inference based on a thermodynamic argument is difficult to interpret in specific molecular terms. As far as we are aware, there is no direct evidence to support existence of such a phase equilibrium.

As noted above, it is possible to observe visually in an equilibrium spreading pressure experiment that all the initially solid polymer dissolves. Thus while it would be tempting to interpret ΔH in eq 5 in terms of a heat of fusion, as is customary in experiments involving small insoluble crystalline amphiphiles,[23] such an analysis does not appear to be justified because an equilibrium between the spread state and the crystalline state does not appear to hold.

Structure of the Surface Film. Molecular models suggest that the PEO monolayer is close-packed at Γ_0 = 0.45 mg/m^2 (16 Å^2/segment).[14] This estimate is inevitably uncertain quantitatively in view of the unknown extent to which the monolayer is strictly two-dimensional and the unknown compressibility of a two-dimensional layer.[19] All the same, the present experiments appear to follow the variation of surface pressure with surface coverage from submonolayer coverage to, nominally, at least 5 layers.

Beyond a surface concentration corresponding to approximately two layers, the surface pressure ceases to rise when further polymer is added to the interface. That the added polymer may dissolve into bulk solution is suggested by the extravagant contributed rise in π when PEO in a diblock copolymer was anchored to the interface by an insoluble polystyrene block.[17,20] However, it is noteworthy that in the present experiments π did not drift with time in the transition zone, where π is very sensitive to surface concentration. This suggests that at least at this level of coverage, dissolution does not take place on the time scale of the experiment. Further, π is also observed to level off at high coverage for PVAc homopolymer (Figure 6) and poly(n-alkyl methacrylates),[21] which are not notably water-soluble. We suggest that PEO collapses by buckling and looping into the water substrate rather than by dissolving wholesale, but a definitive elucidation of the surface structure at high coverage would require more direct methods of analysis.

Comparison with Other Species. The collapse of other known polymer monolayers is associated with negative $d\pi/dT$, i.e., with differential entropy gain. This is observed for PVAc (Figure 6), poly(dimethylsiloxane),[10] poly(phenylmethylsiloxane)[24] and several poly(n-alkyl methacrylates),[21] but not for PEO.

To interpret this anomalous behavior, various possible influences come to mind. (a) Loss of entropy as chains are progressively confined in two dimensions. The two-dimensional analogue of the Flory–Huggins equation predicts[25] that the entropy of flexible polymer chains should decrease with temperature, somewhat more rapidly than predicted by the two-dimensional ideal gas law, $\pi = \Gamma RT$. At submonolayer coverages, this is opposite to the behavior of PEO. (b) Gain of entropy as flexible polymer chains acquire degrees of freedom by collapse to the three-dimensional state. At high surface coverages this is consistent with behavior of other polymers, as noted in the previous paragraph, but is opposite to the behavior of PEO. (c) Specific hydrogen bonding and solvation interactions within the surface layer. Complex interactions of the PEO repeat unit with water molecules have indeed often been discussed in connection with PEO in aqueous bulk solution[13,26] but are poorly understood in detail. In the present experiments the differential entropy loss is an order of magnitude less than when equilibrium with the crystalline state is in question.[23] The present experiments suggest a degree of ordering of water molecules in the surface region. However, these thermodynamic measurements do not allow a specific molecular interpretation at this time.

Summary and Conclusions

The temperature coefficient of surface pressure, $d\pi/dT$, takes a peculiar sign for PEO monolayers spread on deionized water. This implies that, at submonolayer coverage, entropy is gained with increasing surface coverage and that, at still higher surface coverage, entropy is lost with increasing surface coverage. A positive temperature coefficient of the equilibrium spreading coefficient has, to the best of our knowledge, been observed previously only for the spreading of small insoluble crystalline amphiphiles. This makes sense in terms of equilibrium with the crystalline state, but the reasons cannot be the same in the present system. The observation is, however, consistent with ordering of water molecules around the PEO repeat unit.

Reported elsewhere[27] are experiments showing even larger temperature coefficients of π for PEO on aqueous electrolyte substrates of high ionic strength.

These findings illustrate that a polymer monolayer should not be considered as two-dimensional in all respects. In fact there are at least three relevant interaction parameters: segment–segment (in two dimensions)[6-8] but also segment–air and segment–substrate. For PEO monolayers spread on deionized water, the segment–substrate interaction appears to vary with surface coverage.

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