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Notes

Test of Scaling Laws Describing the Concentration Dependence of Surface Pressure of a Polymer Monolayer

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Many polymers are known to spread at the air-water interface as a monolayer.[1-4] The influence of temperature on the compression isotherms of polymer monolayers has been studied. At low surface concentrations C, surface pressure π may be expressed by[5,6]

$$\pi/C = RT(1/M_n + A_2C + ...) \tag{1}$$

where M_n is the number-average molecular weight of the polymer and A_2 is the second virial coefficient. At the Θ temperature, $A_2 = 0$ and eq 1 reduces to the ideal gas law. However, this equation is no longer valid when strong interactions between polymer chains exist. Above the concentration of first contact between chains, $C^* \sim M/R_2^2$, where M is molecular weight and R_2 the radius of gyration of an isolated polymer chain in two dimensions, the relation between surface pressure and surface polymer concentration is expressed, according to the scaling laws,[7-9] by

$$\pi \sim C^y \tag{2}$$

with

$$y = 2\nu/(2\nu - 1) \tag{3}$$

where ν is a characteristic critical exponent to express the radius of gyration in the form $R_2 \sim M^\nu$. Recent calculations showed that $R_2 \sim M^{0.77}$ for good solvents[10] and $R_2 \sim M^{0.505}$ for Θ solvents.[11] Then the y value becomes 2.85 for good solvents and 101 for Θ solvents. Therefore, measurements of π as a function of C yield the exponent ν. Vilanove and Rondelez[9] have attempted to prove the scaling laws by measurements of surface pressures of poly(vinyl acetate) and poly(methyl methacrylate) at an air-water interface at 16.5 °C. The air-water interface at 16.5 °C was a good solvent for poly(vinyl acetate) and a Θ solvent for poly(methyl methacrylate). The exponent y was 2.70 for poly(vinyl acetate) and 10.0 for poly(methyl methacrylate). The experimental value of $\nu = 0.79$ for poly(vinyl acetate) is in good agreement with $\nu = 0.77$ predicted by scaling laws, while the experimental value of $\nu = 0.56$ for poly(methyl methacrylate) is considerably larger than 0.505. Vilanove and Rondelez concluded that this deviation is due to the three facts: First, monomer-monomer interactions are neglected in the scaling laws. Second, the polymer chain is partially submerged in the water subphase upon compression. Last, the air-water interface at 16.5 °C is not truly a Θ solvent.

In this note, in place of using different polymers, we measured the compression isotherms of monolayers of fractionated poly(methyl acrylate) at the air-water interface as a function of temperature, and the exact Θ temperature was determined. The surface pressures were measured under both Θ and good-solvent conditions. The results are compared with the scaling descriptions.

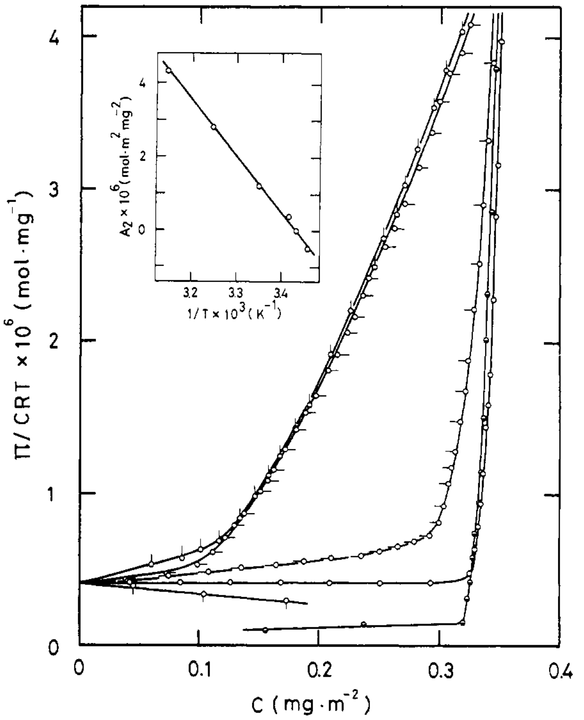

Figure 1. Plots of π/CRT against C at different temperatures: (ȯ) PMA-1 at 45 °C; (o-) PMA-1 at 25 °C; (-o) PMA-1 at 19.5 °C; (o) PMA-1 at 18.2 °C; (ọ) PMA-1 at 16.5 °C; (◒) PMA-2 at 18.2 °C. Insert illustrates the second virial coefficients A_2 as a function of $1/T$.

Experimental Section

Samples. Poly(methyl acrylate) (PMA) was fractionated from its acetone solution using water as a precipitant. Each fraction was dissolved in acetone, precipitated by water, and freeze-dried from a benzene solution. Two fractions were selected. The number-average molecular weight, M_n, for PMA-1 was determined as 2.70×10^3 with a Knauer vapor pressure osmometer in benzene at 30 °C, and M_n for PMA-2 was determined as 30.2×10^4 with a Hewlett-Packard 502 high-speed membrane osmometer in toluene at 30 °C.

Surface Balance. The surface pressures of the spread PMA monolayers were measured by the Wilhelmy technique using a glass plate attached to a sensitive torsion balance. The sensitivity was $\pm 4 \times 10^{-5}$ N/m. A Teflon trough (0.16 m × 0.90 m × 0.01 m) was used. Double-distilled benzene was used as a spreading solvent and double-distilled water was used as the substrate. Spreading of the PMA on the water surface was carried out by applying with a Terumo microsyringe 10-μL benzene solutions (0.5 mg/mL) of the polymers. Compression of monolayers was carried out successively. For a specified temperature, the temperature of the substrate was controlled within 0.05 °C.

Results and Discussion

In Figure 1, π/CRT is plotted against C at different temperatures. Data points at 35 °C are not plotted since they are close to those at 45 °C in the higher concentration range. The initial slope of the plot of π/CRT vs. C decreases with decreasing temperature.

The intercept obtained by extrapolation of π/CRT to $C = 0$ gives M_n. For PMA-1, M_n was 2.4×10^3 and its value is in good agreement with $M_n = 2.70 \times 10^3$ determined by vapor pressure osmometry. For PMA-2, M_n could not be

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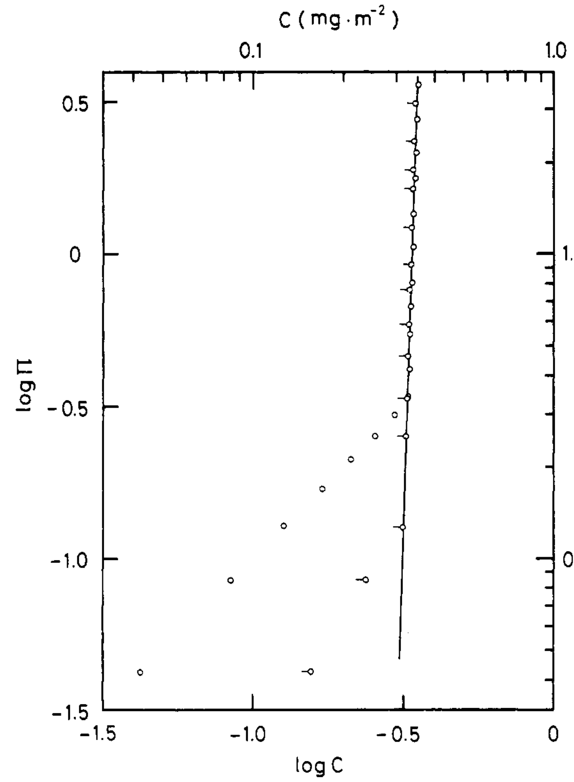

Figure 2. Double-logarithmic plots of surface pressure and surface polymer concentration at the Θ temperature, 18.2 °C: (○) PMA-1; (-○) PMA-2.

determined due to the lack of data at much lower surface pressure. The second virial coefficient determined from the initial slope obtained was plotted against the inverse of the absolute temperature as illustrated in the insert of Figure 1. A straight line with a negative slope was obtained and the Θ temperature for poly(methyl acrylate) is determined as 18.2 °C, which is a little lower than 19.5 °C reported by Llopis and Subirana.[6] It can be seen that, at high concentration, π/CRT increases quite steeply at the Θ temperature.

In Figure 2, the surface pressures measured at the Θ point are plotted against the surface polymer concentration on a double-logarithmic scale. Data points at high concentration for both polymers fall on the least-squares straight solid line with the slope of 35. The limit of error on the slope is found to be 35 ± 5. At low concentration, data points deviate from this solid line. From $y = 35$ the exponent ν is obtained as 0.51 ± 0.005. This value is very close to the theoretical value of 0.505. Moreover, the crossover concentration between dilute and semidilute regimes, C^*, is obtained as 0.32 mg/m^2 for both polymers. This result is reasonable since $C^* \sim M/R_2^2 \sim a^{-1}$ if $R_2 \sim M^{0.50}$, with a the monomer length. The value of C^* gives R_2 = 2.11 nm for PMA-1 and R_2 = 22.3 nm for PMA-2.

Figures 3 and 4 show double-logarithmic plots of the surface pressures at 25, 35, and 45 °C, which correspond to a good-solvent condition, vs. the surface polymer concentration for PMA-1 and PMA-2, respectively. Above C = 0.146 mg/m^2 for PMA-1 and C = 0.128 mg/m^2 for PMA-2, all data points fall on the least-squares straight line with the slope of 2.85 independent of temperature. The limit of error on the slope is found to be 2.85 ± 0.05. This value is in complete agreement with the predictions of the scaling laws.

In conclusion, the surface pressures of poly(methyl acrylate) monolayers in the semidilute regime are in complete agreement with the description of the scaling laws for good- and Θ-solvent conditions, respectively.

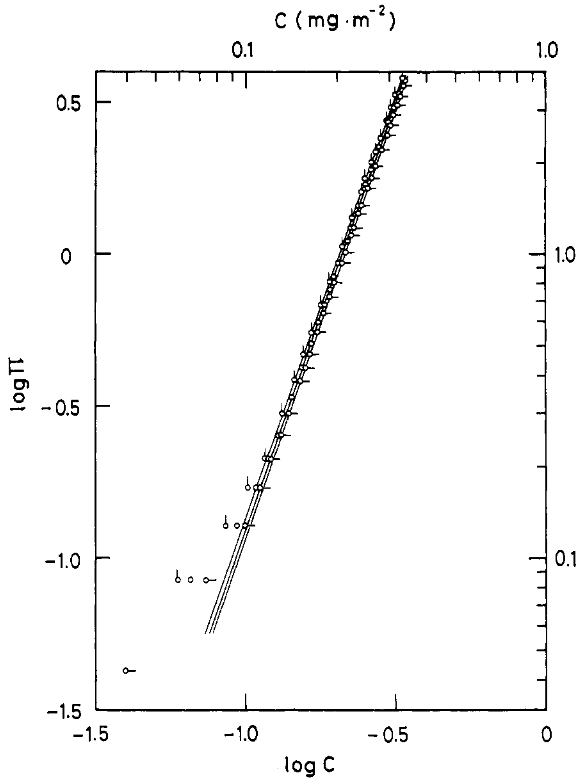

Figure 3. Double-logarithmic plots of surface pressure and surface polymer concentration at 25, 35, and 45 °C for PMA-1: (○-) 25 °C; (○) 35 °C; (ȯ) 45 °C.

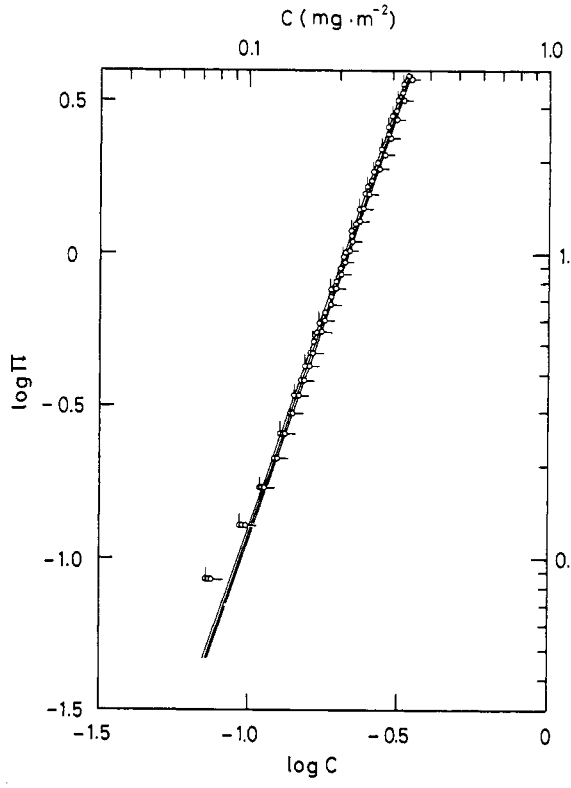

Figure 4. Double-logarithmic plots of surface pressure and surface polymer concentration at 25, 35, and 45 °C for PMA-2. Symbols are the same as in Figure 3.

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Reinvestigation of the Reaction between Triethylsilanol and Trimethylmethoxysilane

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Recently, a report appeared concerning the reaction of triethylsilanol with trimethylmethoxysilane as a model for the reaction of a glass surface with a silane coupling agent.[1] A surprising result of that study was that Et_3SiOH and Me_3SiOMe reacted instantaneously upon mixing at room temperature in the absence of a catalyst. All previous reports had indicated that more vigorous conditions or the presence of a catalyst would be necessary to effect this reaction.[2,3]

We have reexamined the reaction between Et_3SiOH and Me_3SiOMe and have concluded that they do *not* react spontaneously at room temperature. We have shown that the presence of a chlorosilane contaminant, which may have been undetected in the previous study, will cause a fast reaction to occur.

Dreyfuss reported that within 10–15 s of mixing Et_3SiOH and Me_3SiOMe at room temperature, the solution became cloudy and phase separation soon occurred. The upper phase contained $Et_3SiOSiMe_3$ and the lower phase contained methanol (eq 1). When we repeated this experiment, no cloudiness or phase separation was observed and GC analysis indicated no reaction occurred over the course of several days at room temperature. Indeed, when equimolar amounts of Et_3SiOH and Me_3SiOMe were mixed, sealed in a glass ampule, and heated at 60 °C for a week, no reaction occurred.

$$Me_3SiOMe + Et_3SiOH \rightarrow Me_3SiOSiEt_3 + MeOH \qquad (1)$$

A systematic investigation was carried out to discover the source of the discrepancy of observed reactivity. One possibility was that the reactants we used were contaminated with an inhibitor. Alternatively, the reactants employed by Dreyfuss may have been contaminated with a catalyst for the reaction.

The Me_3SiOMe, which was a commercial material distilled from K_2CO_3 prior to use in our studies, was >99% pure by GC analysis. Its elemental analysis was correct and established that it contained <0.1% Cl. The Et_3SiOH employed in our studies was prepared via the hydrolysis of Et_3SiH. The product contained 98% triethylsilanol and 2% hexaethyldisiloxane by GC analysis. The elemental analysis was correct and showed that the sample contained no Cl. The glassware used in our studies was new and was used as received. We conclude that our reactants were pure and did not contain an inhibitor for the reaction.

The reactants used by Dreyfuss were not pure. The Me_3SiOMe reportedly contained 14% $(Me_3Si)_2O$ even after distillation and the Et_3SiOH, which was a commercial material used as received, contained 12% $(Et_3Si)_2O$.

To determine whether a disiloxane could act as a catalyst in the condensation reaction, we added $(Me_3Si)_2O$ (14%) to Me_3SiOMe before mixing with Et_3SiOH. As expected, no reaction occurred even when the reactants were heated. Therefore it seems unlikely that a disiloxane acted to accelerate the condensation reaction in the Dreyfuss studies.

During earlier work in our laboratories, it was found that commercially available silyl ethers often contain impurities that make them highly reactive toward silanols. These impurities generally could not be removed either by simple distillation or by distillation from K_2CO_3. Since silyl ethers are prepared from chlorosilanes, the contaminants were likely to be residual chlorosilanes. Indeed, treatment of these impure silyl ethers with aqueous $AgNO_3$ gave an AgCl precipitate, indicating the presence of active chloride. HCl would be generated upon reaction of a chlorosilane impurity with silanols. HCl is known to be a catalyst for the reaction of silanol with methoxysilane and thus the high reactivity could be explained as a result of the in situ generation of a reaction catalyst.

It appears that the Me_3SiOMe used by Dreyfuss was contaminated with a chlorosilane, probably Me_3SiCl, in addition to the $(Me_3Si)_2O$ contaminant. In an attempt to verify this, various amounts of Me_3SiCl were added to Me_3SiOMe before mixing with Et_3SiOH, and the time lapse from mixing to appearance of cloudiness was noted. When the Me_3SiOMe contained 20–25% Me_3SiCl, a cloudy solution formed within 10–15 s after mixing with Et_3SiOH, just as Dreyfuss described. To see if the same result would be obtained when the Dreyfuss experimental procedure is followed, we fractionally distilled a mixture of 65% Me_3SiOMe, 20% Me_3SiCl, and 15% $(Me_3Si)_2O$ through a 5-in. Vigreux column. The fraction boiling at 58–60.5 °C (uncorrected) was combined with Et_3SiOH, and a cloudy solution formed after about 15 s. When the concentration of Me_3SiCl in Me_3SiOMe was lower, the time lapse between mixing with Et_3SiOH and appearance of cloudiness was longer.

It may seem surprising that 20–25% Me_3SiCl in Me_3SiOMe would not have been detected, but we have found that Me_3SiOMe and Me_3SiCl have the same retention time when Dreyfuss' GC conditions (SE-30 column, 60 °C) are used or when an SE-52 column at 60 °C or even at 30 °C is used. Furthermore, the average molecular weight of a 25% Me_3SiCl in Me_3SiOMe mixture is 105.3, which is within experimental error of the 105.5 value obtained from the MC-2 chromatogram in the previous study. On the basis of this evidence, we conclude that the Me_3SiOMe used in that study must have contained a high concentration of Me_3SiCl contaminant, which caused the Me_3SiOMe to appear highly reactive.

In a previous study carried out in our laboratories, an impure sample of Me_3SiOMe that reacted with Me_3SiOH upon mixing at room temperature was purified by refluxing over and distillation from NaOMe. After distillation from NaOMe, the Me_3SiOMe did not react with Me_3SiOH. Distillation of the impure Me_3SiOMe from K_2CO_3 yielded a sample of Me_3SiOMe that still reacted spontaneously with Me_3SiOH. Presumably, K_2CO_3 would remove any acidic impurities but NaOMe would be required to convert chlorosilane impurities to methoxysilane.

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