Competitive Effects in Polymer Adsorption and Exchangeability of Adsorption Layer

Kunio FURUSAWA* and Kazuaki YAMAMOTO†

The University of Tsukuba, Department of Chemistry, Sakura-mura, Ibaraki 305

(Received January 28, 1983)

Critical experimental data on competitive adsorption and exchangeablity of adsorbed polymer are produced under the various conditions using the gel permeation chromatography technique. It is apparent that the competitive effects and the exchangeability were found to depend not only on the molecular weight of the polymer, but also on the concentration of each component at which the corresponding adsorption is carried out. This can be explained as follows; the conformation of the adsorbed polymer would be influenced extensively by the polymer concentration in bulk. The polymer molecules adsorbed from a dilute solution would take on a flat conformation being rich in train segments, but the polymer layer formed under a concentrated solution would occupy a small of sites and adopt an extended loop configuration which would be desorbed more easily than the flat one. Also, in the mixed sample the effects of adsorption Kinetics play an important role on the structure of the adsorption layer, because at first the surface is convered by an adsorption layer of small components due to its rapid adsorption rate.

Among the various branches of surface and polymer chemistry, the problem on polymer adsorption at solid-liquid interface is still new and much attention has been paid to it, both theoretically and experimentally. Especially, the problems on (ir)reversibility of polymer adsorption are fundamental and essential ones, because these are concerned with the thermodynamic background in these approaches.

On the question of whether or not polymer molecules adsorb reversibly on a solid surface, experimental data sometimes give conflicting answers. For example, often no detectable desorption can be observed upon dilution,[1,2] whereas the adsorbed polymer is easily desorbed by altering the quality of the solvent.[3] Similar confusing facts can be observed in the theoretical field.[4] Some theories predict irreversible properties, and others reversible ones.

Recently, Cohen Stuart *et al.*[5] showed that many experimental observations ascribed to irreversibility can be explained in therms of polydispersity of the sample, *i.e.*, in a polydisperse sample, preferential adsorption of a large molecule over a smaller one occurs.[6,7] Especially, with increasing molecular weight(M) the polymers adsorb progressively more strongly and exchanges for molecules of smaller M. If the polymer concentration is increased, larger molecules are available to replace smaller ones. Therefore, the molecular weight distribution on the adsorption layer changes with the amount of adsorption and may differ considerably from that in the bulk phase. This fractionation process continues as long as there are larger molecules in the bulk phase than on the adsorption layer and the adsorption isotherm is strongly influenced by the molecular weight distribution of the sample. Hence, in such an adsorption, it is impossible practically to follow the isotherm back by dilution alone and the process appears to be irreversible.

Under the concept proposed by Cohen Stuart *et al.*, it is important to obtain an exact knowledge of competitive effects of polymer molecules and exchangeability of the adsorbed polymer. In this work, competitive and displacement effects in a polymer adsorption process, were examined in some detail using polystyrene samples with narrow-molecular-weight distribution at the Θ-conditions. Furthermore, much attention has been paid to the effects from adsorption kinetics which were neglected in the Cohen Stuart theory, because at the beginning the adsorption layer of a mixed sample is occupied entirely by the small components due to their rapid adsorption rate. These analyses were performed quantitatively by the gel permeation chromatography technique. We believe that these data will shed some light on the problem of (ir)reversibility of polymer adsorption.

Experimental

Materials. Linear polystyrene samples having a narrow molecular weight distribution were supplied by Toyo Soda Co. Ltd., (Shinnanyo, Yamaguchi, Japan). The characteristics of the samples used are given in Table 1.

Cyclohexane, employed as the theta solvent, was purified by the procedure described in a previous paper.[8] Commercial porous glass beads with a particle size of 120—200 mesh were mainly used as substrate which were supplied by Electron-Nucleonics Inc.(Fairfield, N.J.) and designated as CPG-10. The surface area and the average pore-radius of these beads were reported by the supplier to be 15.0 m^2/g and 1000 A, respectively. The pore radius is about 3—30 time larger than the radius of gyration of the dissolved polymers in cyclohexane at 35 °C. Under these conditions, the effect of the porosity of the adsorbent can be ignored

TABLE 1. CHARACTERISTIC OF POLYSTYRENE SAMPLES

Sample	M_w	M_w/M_n
S-1.7[a]	16 700	1.02
S-5[b]	50 000	1.06
S-10.7[a]	107 000	1.01
S-18.6[a]	186 000	1.07
S-41.1[b]	411 000	1.06
S-77.5[a]	775 000	1.01
S-128[a]	1280 000	1.05
S-200[b]	2000 000	1.06

a) Supplied by Toyo Soda Co. Ltd., (Yamaguchi, Japan).
b) Supplied by Pressure Chemicals (Pittsburg, Pa. U.S.A.).

† Present address: Toyo Soda Co. Ltd., Tonda, Shinnanyo, Yamaguchi 746.

in the adsorption process of these polymers.[9] The glass beads were cleaned carefully by the method described previously.[9]

Adsorption Experiments. The determination of the amount of polymer adsorbed was carried out by measuring the change in concentration of the supernatant liquid using a digital precision density meter(Anton paar. K.G. PHA02C). The temperature of the adsorption tube was controlled within 0.05 °C. The details concerning the adsorption process and the analysis of these data were reported previously.[9]

GPC Measurements. The measurements were carried out with a Toyo Soda Model 803-A GPC at 25 °C, with chloroform as a solvent. The GPC chromatograph was equipped with two 7.5 mm × 600 mm stainless-steel columns, types TKS-DMH and G200H. 0.4-ml portions of the polymer solution with 1.0 to 2.0 g m^{-3} was injected and eluted at 25 °C under a flow rate of 1-ml/min.

Measurements of Competitive Adsorbability. In order to determine the competitive(or preferential) adsorbability between different molecular weight species, adsorption isotherms of mixtures were constructed. The total adsorption amounts of the mixtures were determined by the usual procedure using the density meter. For evaluation of each component in the adsorption layers, the GPC technique was employed. After the adsorption period(usual adsorption time is 24 h), the supernatant solution of the mixture and the original solution were evaporated, and the polystyrene films obtained were subsequently dissolved in benzene for freeze drying. The polymer was allowed to remain to a vacuum line for 12 h in 10^{-3} Torr (1 Torr≈133.322 Pa). Both samples were finally dissolved in chloroform within the concentration range 1.0 to 2.0 g m^{-3} so as to present no appreciable concentration effect on the elution curve. In Fig. 1, an example of GPC chromatograms obtained for both samples is illustrated. The amounts of adsorption for individual components in the binary mixture were calculated by the following relations deduced from a simple mass balance analysis:

$$A_a = A_t(\alpha+\alpha\beta'-\alpha'\beta),$$
$$A_b = A_t(\beta+\alpha'\beta-\alpha\beta'). \quad (1)$$

Here, A_a, A_b, and A_t indicate the amounts of adsorption for the components a, b, and their total, and α, β, α', and β' show the areas of normalized chromatograms for components a and b before and after the adsorption process. For a tertiary mixture, the chromatogram was also analyzed under the same consideration.

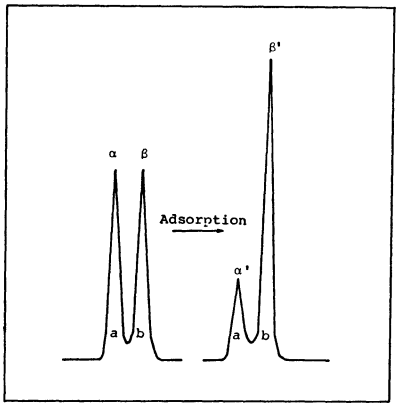

Fig. 1. Gel permeation chromatograms showing relative change of two components before (a,b) and after (a',b') the adsorption process. (α,β), (α',β'): Areas of normalized chromatogram for the components before and after adsorption.

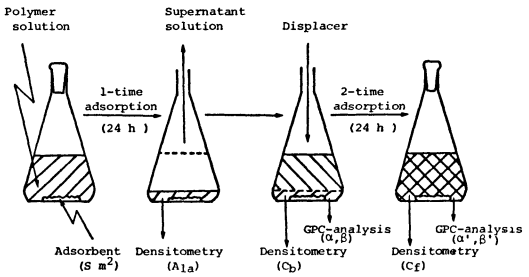

Fig. 2. A schematic picture for showing the procedure to determine the exchangeability of absorption layer.

Measurements of Exchangeability of Adsorption Layer. The exchangeability of the adsorbed polymer was also measured by the GPC technique. A schematic picture of the procedure is shown in Fig. 2. The surface of the adsorbent was first occupied with one polymer species according to the usual adsorption process and then the amounts of adsorption was determined by measuring the residual concentration of the polymer. Thereafter, the supernatant was substituted with another polymer solution used as displacer(usually the concentration of displacer is 35 g m^{-3}). The half-volume of the new supernatant was immediately taken from the tube and after determining the concentration(C_b), the solution was prepared as the GPC sample to analyse the components at the beginning time. Then, the "second-time adsorption" was performed in the other half-volume of the displacer. After the adsorption period of 24 h, the determination of polymer concentration(C_f) and the GPC analysis for the supernatant were conducted in the same way as described above. From these measurements, the adsorption amounts of the total(A_{2t}) and each component(A_{2a}, A_{2b}) in the adsorption layer after completion of the second adsorption process, can be calculated by the following relations which were deduced by a simple analysis and the mass balances,

$$A_{2t} = A_{1a} + \frac{(C_b-C_f)}{S}, \quad (2)$$

$$A_{2a} = A_{1a} + \frac{(C_b-C_f)}{S}(\alpha+\alpha\beta'-\alpha'\beta), \quad (3)$$

$$A_{2b} = \frac{(C_b-C_f)}{S}(\beta+\alpha'\beta-\alpha\beta'). \quad (4)$$

Where A_{1a} is the amount of adsorption for the component "a" after the first-time adsorption, S the total surface area of adsorbent employed, C_b and C_f the total polymer concentrations before and after the second-time adsorption.

Results and Discussion

Adsorption Rate of Mixed Sample. To measure the apparent rate of adsorption, the adsorbed amounts of mixed polymers were determined at various time intervals from 0.1 to 24 h at an initial polymer concentration of 60 g m^{-3} which gives enough saturated amount of adsorption. Figure 3 shows a plot of adsorption rate for a mixture containing two components of different molecular weight samples(S-18.6 and S-77.5) in 1:1 ration. In the same figure, the calculated adsorptions of individual component in the mixture which were determined by the GPC analysis, are also shown. It is seen that the apparent adsorption of

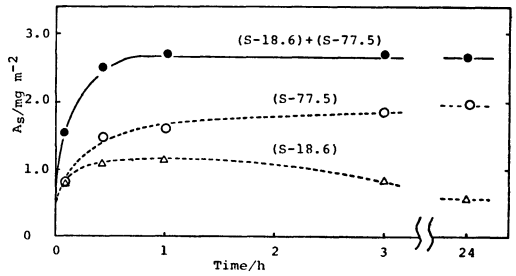

Fig. 3. Adsorption rate of a mixture containing two components (C_p=60 g m^{-3}, in cyclohexane, 35 °C).
(●): Mixture (S-18.7+S-77.5), (△): S-18.6 in mixture, (○): 8-77.5 in mixture.

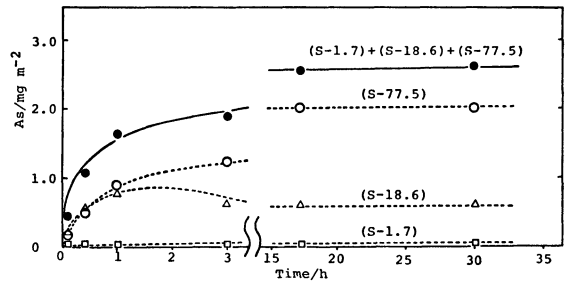

Fig. 4. Adsorption rate of a mixture containing three components (C_p=60 g m^{-3}, in cyclohexane, 35 °C).
(●): Mixture(S-1.7+S-18.6+S-77.5), (□): S-1.7 in mixture (△): S-18.6 in mixture, (○): S-77.5 in mixture.

the mixture reach an equilibrium within 1 h, but the relative change of each component in the adsorption layer continued for a long time. This tendency can be explained by the differences of the adsorption rates of each polymer species. The surface of the adsorbent will be occupied at first by the law molecular weight species because of their rapid adsorption rate and then exchanged by the later arrivals with higher molecular masses, displaying, as a rule preferential adsorbability. In Fig. 4, we have plotted adsorption rates for a mixture containing three components of different molecular weights(S-1.7, S-18.6, and S-77.5) in 1:1:1 ratio. As may be seen in the figure, the time required for attaining real equilibrium is very long and is barely established after 20 h. From these data, we can imagine that an enormous period will be necessary for a polydisperse sample to attain real equilibrium of adsorption.

Competitive Effects of Polymers Having Different Molecular Weights. In Fig. 5, a molecular weight dependence of saturated adsorption, A_s, for a series of different molecular weight species, is shown in the form of a $\log A_s$ *vs.* $\log M_w$ plot. As may be seen in the figure, $\log A_s$ and $\log M_w$ are related by a straight line and the molecular weight dependence parameter for the adsorption(ν=dlog A_s/dlog M_w) was calculated to be ν=0.29$_5$ from the slope of the line. Thus there will be a competitive effect between the different molecular weight species when a mixed sample is used as the adsorbate.

Figure 6 shows an example of an adsorption isotherm for a mixture containing three components of different molecular weights in 1:1:1 ratio. The mixture isotherm shows a round shape as may be expected from the Cohen Stuart's theory and finally tends to an adsorption of the highest-molecular-weight component. In the same figure, the calculated adsorptions of individual components in the mixture are also shown. It appears that the preference for large molecules over smaller ones can be seen over the whole concentration region and the composition of the adsorption layer is much dependent on the solution concentration at which the corresponding adsorption is carried out. However, it is noteworthly that some adsorption of the lowest-molecular-weight species are found over the the whole concentration region. This result suggests that preferential adsorption of large molecules over smaller ones is not complete and the composition of both the bulk and the adsorption layer varies smoothly with the molecular weight of the polymer.

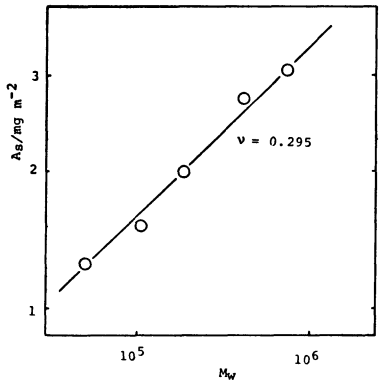

Fig. 5. Molecular weight dependence of saturated adsorption of polystyrene on porous glass from cyclohexane solution at 35 °C.

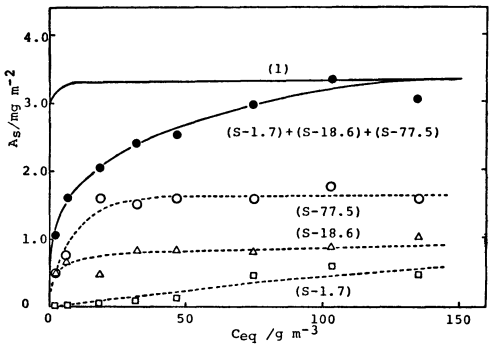

Fig. 6. Adsorption isotherms for a mixture containing three components of different molecular weights (in cyclohexane, 35 °C).
(○): Mixture (S-1.7+S-18.6+S-77.5), (□): S-1.7 in mixture, (△): S-18.6 in mixture, (○): S-77.5 in mixture.

Exchangeability of the Adsorption Layer. From analysis of the exchange process of one adsorbed polymer by another, we can get much knowledge on the peculiarity of polymer adsorption. Figures 7, 8, and 9 show the results for three combinations of different molecular weight species. In these figures, demonstrating the degree of displacement of adsorption layers formed under the various residual concentrations (C_{eq-1}) by a definite displacer solution(usually we

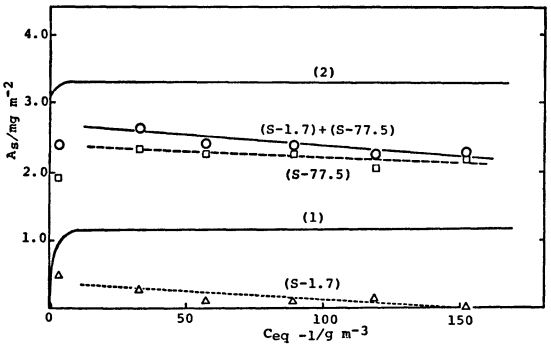

Fig. 7. Exchangeability of adsorption layers formed under the various equilibrium concentrations of primal adsorbate (C_{eq-1}) by a definite displacer solution ($C_{dis.}$: 35 g m^{-3}).
(○): Total adsorption amounts after 2-time adsorption, (△): residual amounts of adsorbate after 2-time adsorption, (□): exchanged amounts of displacer after 2-time adsorption, (1): adsorption isotherm of primal adsorbate (S-1.7), (2): adsorption isotherm of displacer (S-77.5).

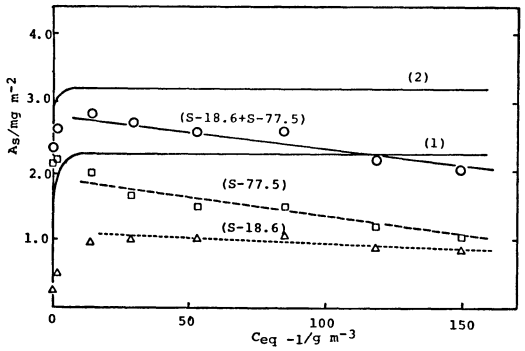

Fig. 8. Exchangeability of adsorption layers formed under the various equilibrium concentrations of primal adsorbate (C_{eq-1}) by a definite displacer solution ($C_{dis.}$: 35 g m^{-3}).
(○): Total adsorption amounts after 2-time adsoption, (△): residual amounts of adsorbate after 2-time adsorption, (□): exchanged amounts of displacer after 2-time adsorption, (1): adsorption isotherm of primal adsorbate (S-18.6), (2): adsorption isotherm of displacer (S-77.5).

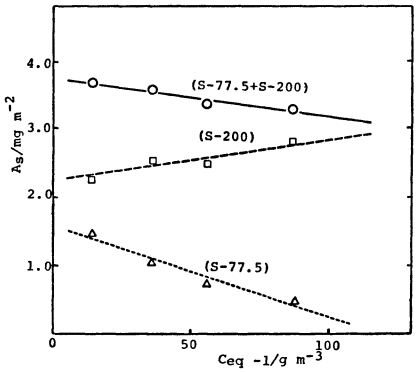

Fig. 9. Exchangeability of adsorption layers formed under the various equilibrium concentrations of primal adsorbate (C_{eq-1}) by a definite displacer solution ($C_{dis.}$: 35 g m^{-3}).
(○): Total adsorption amounts after 2-time adsorption, (△): residual amounts of adsorbate after 2-time adsorption, (□): exchanged amounts of displacer after 2-time adsorption.

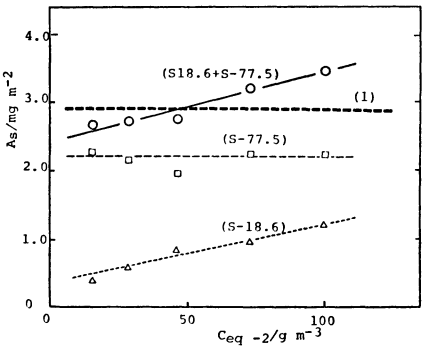

Fig. 10. Exchangeability of adsorption layer of big molecules (S-77.5) formed under a definite concentration (C_{eq-1}=27 g m^{-3}) by different concentrated solutions (C_{eq-2}) of small molecules (S-18.6).
(○): Total adsorption amounts after 2-time adsorption, (△): residual amounts of adsorbate after 2-time adsorption, (□): exchanged amounts of displacer after 2-time adsorption, (1): line showing adsorption amount of primale adsorbate, (S-77.5).

fixed the concentration at 35 g m^{-2}). For the sake of comparison, Figs. 7 and 8 include isotherms of the adsorbate and the displacer themselves. As may be seen from these figures, the small component adsorbing on the surface is displaced extensively by the large-size molecules used as a displacer. The degree of displacement is greatly dependent on the difference of molecular weights of both polymers: *i.e.*, in a much different combination(Fig. 7), the degree of displacement is extensive and in the small differences(Figs. 8 and 9), the degree is not so extensive. A striking feature seen from these figures is that the exchangeability is found to depend not only on the molecular weight of the adsorbed polymer but also on the solution concentration at which the corresponding initial adsorption was carried out. It appears that the polymer molecules adsorbed at high concentrations are exchanged more easily than the polymer layer formed at low concentrations. If the exchangeability is related to the number of adsorbed segments, this suggests that the polymer layer formed at high concentrations has smaller adsorbed segments than the layer formed at low concentrations. This can be explained by the polymer molecules in a dilute solution arriving at the sparsely populated surface and adopting a relatively flat conformation; however the polymer molecules in a more concentrated solution, especially when some later arrivals come to the surface, would occupy a smaller number of sites and therefore must adopt a considerably extended loop conformation which would be desorbed more easily than the flat ones. Also, it is interesting to notice that the total adsorbances after the second-time adsorption show an increasing tendency with decreasing the equivalent concentrations of the displacer. This will be due to different couples of residual molecules with a flat conformation and dis-

placed molecules with an extended conformation.

Another peculiarity in the polymer adsorption is shown in Fig. 10, where the large molecules adsorbed previously are exchanged by a displacer having a small molecular weight, though such a trend is not as pronounced as those found in the opposite combination. However, this result shows crucially that the preference in polymer adsorption depends not only on the molecular weight of the adsorbate, but also on the solution concentration of each species. Furthermore, Fig. 10 shows another indication that the big molecules remaining in the adsorption layer are maintained constant over the whole concentration region of the displacer. This shows that there are "weakly adsorbed matters" in the adsorption layer(*ca.* 25%) and they are classified essentially with the other firmly adsorbed components. Existence of the "weakly adsorbed matters" were also found by Terashima *et al.*[10] in their direct adsorption measurements using microbalance.

In this article, we have attempted to produce critical experimental data on the competitive effects in the polymer adsorption and exchangeability of the adsorption layer. All these data support the Cohen Stuart's theory and are well explained by the concept of reversible adsorption of the polymer.

References

1) W. H. Grant, L. E. Smith, and R. R. Stromberg, *Faraday Discuss. Chem. Soc.*, **59**, 209 (1975).

2) G. J. Howard and P. Mc Connel, *J. Phys. Chem.*, **71**, 2981 (1967).

3) M. Kawaguchi and A. Takahashi, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 2069 (1980).

4) J. M. G. Lankveld and J. Lyklema, Vth Intern. Congr. Surface Activity (Barcelona), Proceeding Vol. 2, 633 (1968); L. K. Koopal and J. Lyklema, *Faraday Discuss. Chem. Soc.*, **59**, 230 (1975).

5) M. A. Cohen Stuart, J. M. H. M. Scheutjens, and G. J. Fleer, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 559 (1980); M. A. Cohen Stuart, Thesis, Agricultural University, Wageningen, The Netherlands, 1980.

6) C. Vander Linden and R. Van Leemput, *J. Colloid Interface Sci.*, **67**, 63 (1978).

7) G. J. Howard and S. J. Woods, *J. Polym. Sci., Part A-2*, **10**, 1023 (1970).

8) K. Furusawa, H. Nakanishi, and K. Kotera, Intern. Conf. Colloid and Surface Science(Budapest), Proceeding Vol. 1, 221 (1975).

9) Kunio Furusawa, K. Yamashita, and K. Konno, *J. Colloid Interface. Sci.*, **86**, 35 (1982).

10) H. Terashima, J. Klein, and P. F. Luckham, "Adsorption from Solution," ed by R. H. Ottewill, C. H. Rochester, and A. L. Smith, Academic Press, London (1983), p. 299.