

Some Singularities of Polystyrene Adsorption on Technical Carbon

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Abstract

Investigation of filled composite materials is connected with polymer adsorption on a solid surface. Studies of adsorption from polymer solutions on solid surfaces are mainly aimed at revealing how the value of adsorption depends on the thermodynamic quality of the solvent, polymer concentration in the solution, molecular mass and molecular-mass distribution of polymer, temperature, nature of adsorbent, and surface charge and charge density, in polyelectrolytes. The adsorption systems containing macromolecules and dispersed particles of the solid phase are rather complex, because they have features of both lyophobic and lyophilic disperse systems.

We studied adsorption of polystyrene with molecular mass 5.7×10^5 from a solution in toluene on three samples of commercial-grade carbon: TM-15, TM-50, and TM-75 with specific surface area equal to 15, 50 and 75 m²/g, respectively, under various experimental conditions. The carbon powder was preliminarily dispersed in a particular volume of solvent, and this dispersion was mixed with an equal volume of solution and a double concentration of polymer.

Preliminary dispersion of technical carbon in solvent influences on an adsorption process. In this connection the solvent concentration, under which non-separated technical carbon particles are appeared, is decreasing.

Introduction

Studies of adsorption from polymer solutions on solid surfaces are mainly aimed at revealing how the value of adsorption depends on the thermodynamic quality of the solvent, polymer concentration in the solution, molecular mass and molecular-mass distribution of polymer, temperature, nature of adsorbent, and surface charge and charge density in polyelectrolytes. The adsorption systems containing macromolecules and dispersed particles (DP) of the solid phase are rather complex, because they have features of both lyophobic and lyophilic disperse systems. Naturally, the two components with opposite aggregation properties affect each other, causing transition of the system from the initial state characterized by two dissimilar equilibria established for each component to the final state with a common equilibrium in the system. Such transitions

and the ratio between their rates determine the value of adsorption.

We studied adsorption of polystyrene with molecular mass 5.7×10^5 from a solution in toluene on three samples of commercial-grade carbon: TM-15, TM-50, and TM-75 with specific surface area equal to 15, 50, and 75 m²/g, respectively, under various experimental conditions. Adsorption was studied by two procedures with different initial development of aggregation processes: (1) the solution with predetermined polymer concentration was mixed with a particular amount of initial dry adsorbent (carbon), and (2) the carbon powder was preliminarily dispersed in a particular, volume of solvent, and this dispersion was mixed with an equal volume of solution and a double concentration of polymer.

Hence, the ratio between the concentrations of polymer and solid phase and the equilibrium volume of the adsorption system were the same in both procedures, and we only changed the initial conditions of dispersion of carbon powder and initial equilibrium between individual macromolecules and their aggregates in the polymer solution. After the adsorption equilibrium was established (in a day), we separated the system by filtration and determined the mass of adsorbed polymer by gravimetry. In addition, we studied the light transmission of the equilibrium polymer solutions after adsorption, because we discovered that separation was incomplete. Figure 1 represents the results obtained.

Studying the sediments, we indirectly estimated the aggregation stability of the carbon samples and the influence of macromolecules on this stability (Fig. 2). The aggregation stability in the pure solvent decreased in the order TM-75 > TM-50 > TM-15.

The presence of DP of solid phase in the adsorption system can cause errors in the measurements of equilibrium polymer concentration after adsorption. These errors may have two origins. First, the DP of the solid phase penetrated into the macromolecular aggregates may remain in the equilibrium polymer solution after its separation, thus leading to overestimation of polymer concentration.¹ Secondly, the DP of the solid phase may form local coagulation structures with the pores filled with the solvent, which are inaccessible for macromolecules. This effect also increases the polymer concentration in equilibrium solution. Both these processes can take place simultaneously.²

Our studies of light transmission of the equilibrium polymer solutions after adsorption showed that transmittance begins to decrease after a certain polymer concentration is attained. Therefore, the carbon particles are not completely separated from the solution (Fig. 1b). Due to the presence of dispersed carbon particles in equilibrium polymer solutions after separation of sediment, the methods used to determine the polymer concentration in solution overestimate the polymer concentrations and, correspondingly, underestimate the adsorption of polymer. The polymer concentrations at which the carbon particles are left in the equilibrium polymer solutions decrease as one passes from TM-75 to TM-15. If carbon was preliminarily dispersed, these concentrations also decrease, i.e., a larger correction must be made to the value of adsorption measured in this case. Such corrections can be made from the calibration plots of suspension transmittance versus carbon concentration.

The equilibrium adsorption system contains local porous coagulation structures filled with the solvent. This is the second cause that complicates adsorption and leads to errors in determination of the adsorption value. In this case, the solvent is trapped by forming coagulation structures and redistributed between solid and liquid phases of the adsorption system. Macromolecules may also be trapped together with the solvent.

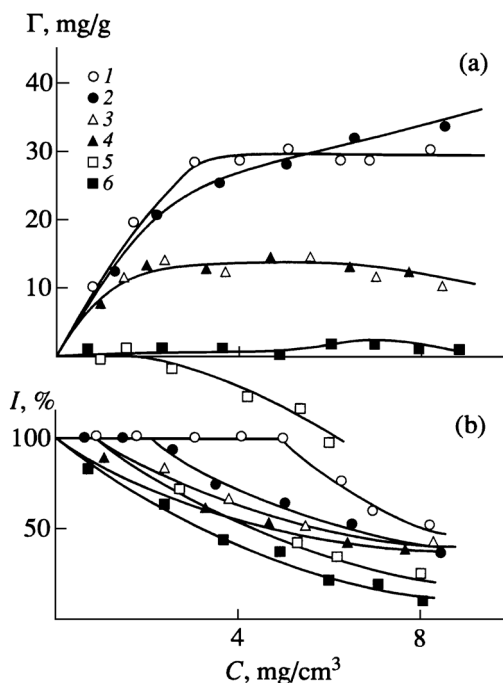


Figure 1. Dependences of (a) values of adsorption and (b) light transmittance of equilibrium polymer solutions after adsorption on the equilibrium polymer concentration for the following samples of carbon: (1,2) TM-75, (3,4) TM-50, and (5,6) TM-15.

The experiments on adsorption were performed by (1,3,5) the first and (2,4,6) the second procedures described in the text.

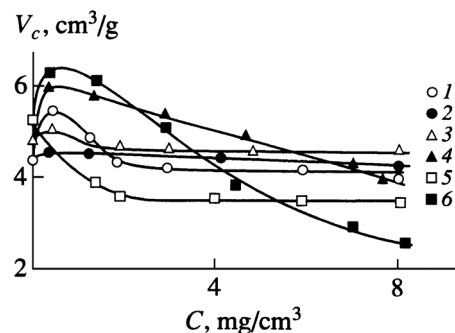


Figure 2. Dependences of coagulation volume (V_c) on the equilibrium polymer concentration for the following samples of carbon: (1,2) TM-75, (3,4) TM-50, and (5,6) TM-15.

The experiments on adsorption were performed by (1,3,5) the first and (2,4,6) the second procedures described in the text.

With respect to the solid phase, an experiment on adsorption should also be considered as a process of disaggregation of powder particles in polymer solution. It is useful to discuss the following four cases: (1) the DPs are completely disaggregated, and adsorption of macromolecules enhances the aggregation stability of these particles; (2) the DPs are completely disaggregated, and adsorption of macromolecules reduces the aggregation stability of these particles, thus causing flocculation; (3) the DPs are partially disaggregated and form aggregates of a certain size, and adsorption of macromolecules enhances the aggregation stability of these particles; and (4) the DPs are partially disaggregated and form aggregates of a certain size, and adsorption of macromolecules reduces the aggregation stability of these particles.

In the first case, disaggregation of the DPs to individual particles and stabilization of these particles by the adsorbed macromolecules cause significant values of limiting adsorption, which do not depend on the pattern of mixing the components. Preliminary disaggregation of DPs may just accelerate the equilibration.

In the second case, disaggregation of the DPs to individual particles and their flocculation by the adsorbed macromolecules lead to the formation of various coagulation structures. In this case, the value of limiting adsorption substantially depends on the ratio between the rates of disaggregation of the DPs and their flocculation caused by polymer adsorption on these particles. Preliminary disaggregation of particles enhances adsorption of macromolecules.

Let us consider the third case. If the solvent does not facilitate disaggregation of the DPs and if adsorption of macromolecules enhances the aggregation stability of these particles, then one may observe an adsorption isotherm slowly reaching a plateau or an isotherm without saturation. It is difficult to find out whether the adsorption saturation is attained in such systems.

The fourth case implies that disaggregation of DPs in the solvent is incomplete and the particles lose their stability on adsorption of macromolecules. Apparently, this is the most common case for flocculation of dispersions by polymers. This pattern can explain significant friability of flocculated sediments, which is determined by the friability of the aggregates of DPs and the friability of the forming structure.

With respect to the polymer solution, an experiment on adsorption can be considered as adsorption of individual macromolecules and their aggregates. The proportion between these species is determined by the nature of polymer and solvent, and by concentration of macromolecules.³ As the concentration of polymer in solution rises and the equilibrium "individual macromolecules \leftrightarrow macromolecular aggregates" shifts to aggregates, the equilibration time increases and the influence of macromolecules on the aggregation stability of particles and formation of coagulation structure is changed. The shift of equilibrium to aggregates is more pronounced when one follows the second procedure of experiments instead of the first one. This fact can explain why a more friable coagulation structure is formed at low polymer concentrations, when adsorption on TM-15 is studied by the second procedure or adsorption on TM-75 is studied by the first procedure (Fig. 2). We also note that the concentration, corresponding to the appearance of carbon particles that cannot be separated from the solution, is lower when one passes from the first procedure of the experiments on adsorption to the second one (Fig. 1b). Possibly, this is the case because such particles may appear when the solution contains macromolecular aggregates of a certain size.¹

Conclusion

Hence, when one studies the adsorption of polymers on dispersed adsorbents, the classical concept of adsorption as

the variation of the substance concentration near the interface is indefinite because the sizes of adsorbent and adsorbate are comparable. Then, it is more correct to speak of aggregation of the DPs of adsorbent and adsorbate. The properties of these aggregates depend on the proportion between the interacting components. Analyzing the effects discussed, we see that sometimes one cannot use the experimental values of Γ to characterize the affinities of adsorbent and adsorbate. Rather, these values may be used to estimate the kinetic control of polymer adsorption.

References

1. I. E. Opainich, I. I. Maleev and G. B. Semchishin, *Vestn. Lvovskogo Univ., Ser. Khim.*, **30**, 30 (1989).
2. I. I. Maleev, M. N. Soltys, I. E. Opainich and Z. M. Yaremko, *Adsorption and Chromatography of Elastomer Macromolecules, Materialy 3 Vsesoyuznogo seminaru po adsorbtsii i zhidkostnoi khromatografii elastomerov (Proc. 3rd All-Union Seminar on Adsorption and Liquid Chromatography of Elastomers)*, Moscow, pg. 24. (1992).
3. Yu. S. Lipatov, Z. M. Yaremko and M. N. Soltys, *Dokl. Akad. Nauk SSSR*, **319**, 910 (1991).

Biography

Iryna Opaynych received her M.S. in Physical Chemistry from the University of L'viv in 1965, and her Ph.D. in Chemistry from the University of L'viv in 1983. Dr. Opaynych is current an associate professor of chemistry at the chemical faculty of the L'viv University. She has published over one hundred papers, including inventions, one of inventions has been patented in USA, France, UK, Japan and others countries. Iryna Opaynych works in the area of polymeric composite materials chemistry.