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Adsorption of mixtures of polymers from dilute and semidilute solutions

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Abstract. Recent studies of adsorption from solutions of mixtures of polymers have been examined. The experimental results reveal an interrelation between the adsorption of polymers from a mixture, the thermodynamic compatibility of the components in solution, the change in the thermodynamic quality of the 'mixed solvent' (polymer + solvent), and the critical crossover concentration for each component (on the one hand) and the averaged critical concentration for the mixture. The influence of the aggregation of macromolecules in solutions of mixtures on the adsorption in the concentration regions above and below the critical concentration for the overlapping of macromolecular globules has been demonstrated. The bibliography includes 30 references.

I. Introduction

According to current views on the properties of solutions of polymers these solutions can be divided into dilute and semidilute.[1] In a dilute solution the macromolecular globules are separated in space, but when the critical concentration c^* (and therefore the critical volume fraction of polymer φ) is reached the globules begin to come into contact and they overlap. The concentration region in which the globules overlap (the cross-over region) corresponds to the local concentration within the globule, giving a solution concentration $\varphi^* < \varphi < 1$. The overlapping is accompanied by a compression of the globules and by a decrease in their size. The critical concentration c^* is determined by the molecular mass of the polymer and by the thermodynamic quality of the solvent. Various theoretical models have been proposed to determine the concentration c^*: according to them this quantity is inversely proportional to the characteristic viscosity $[\eta]$, and the proportionality coefficient depends on the model chosen for the interaction of the globules.[2–6]

Many published data show that macromolecular associations or aggregates with a long average lifetime can be formed in solutions of polymers, depending on their concentration and on the thermodynamic quality of the solvent.[7,8] The size of the aggregates is also determined by the molecular mass and by the nature of the solvent. In solutions of any concentration we find a mobile equilibrium between the aggregated and the free macromolecules. From the standpoint of classifying the solutions into dilute and semidilute it is evident that the aggregation processes should begin in a dilute solution and stop at the transition to a semidilute solution, where all the macromolecules overlap and create a network.

In a series of studies in our laboratory[7,9] the conditions for the formation of aggregates, their size, and number per unit volume have been determined. Comparing these data with the results of adsorption studies (from solutions) led to the formulation of the concept of aggregative adsorption.[10,11] Essentially this concept states that in an appropriate concentration region of the solution, in which macromolecular aggregates are formed, both aggregated and nonaggregated macromolecules are simultaneously transferred to the adsorbent surface during adsorption, but the transfer of the molecular aggregates is energetically more favourable. As a result there are almost no aggregates in the solution over the adsorbent after the adsorption equilibrium has been established, but after some time their equilibrium concentration in the solution is re-established.

The aggregative adsorption mechanism has provided an explanation for several experimental data which did not fit the traditional description of adsorption from dilute solutions,[12,13] such as large adsorptions, well in excess of the calculated monolayer value, with a relatively small proportion of segments bound to the surface, an inversion of the effect of the thermodynamic quality of the solvent on the adsorption following changes in concentration, a dependence of the adsorption on the adsorbent : solution ratio, etc.[7] In the aggregative adsorption mechanism the large difference between the adsorption of polymers and the adsorption of species of low molecular mass is stressed.[10] In the adsorption of polymeric molecules not only the conformation of the adsorbed molecules but also the size and number of the macromolecular aggregates depend on the concentration of the solution, so that at different points of the adsorption isotherm we are dealing with different ratios of these species in the solution. From this point of view it is interesting to consider the adsorption of mixtures of polymers from dilute and from semidilute solutions, in which the aggregation conditions of polymer molecules of each kind should be different. It may be assumed that the adsorption of a mixture of polymers from a common solvent is affected by their thermodynamic compatibility (or noncompatibility) in the solution, defined by the thermodynamic polymer–polymer interaction parameter.

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A large group of experimental data on the adsorption of mixtures of polymers is now available.[14-19] In most cases a marked selectivity of the adsorption of one of the components is observed in the adsorption from a mixture. When this effect was first reported[14-16] it seemed reasonable to assume that a noncompatible pair of polymers in solution would also show a more marked segregation of identical macromolecules, i.e. a more marked aggregation. This effect should depend on the overall concentration of the components in solution, on the concentration ratios, and on the concentration of each component (with respect to the remoteness from or closeness to the crossover region for the given polymer).

An analysis of all the available data showed that the adsorption of polymers should be examined from the following standpoints. A solution of a mixture of two polymers in a common solvent can be described as a solution of the polymer A in a solution of the polymer B in the same solvent, and also as a solution of the polymer B in a solution of the polymer A. In this case the thermodynamic quality of the 'mixed' solvent (solvent + polymer) for each polymer will be different from the quality of the pure solvent. The adsorption of each polymer will depend on the influence of the other polymer on the thermodynamic quality of the 'mixed' solvent. Thus the adsorption of each component will be determined not only by the affinity of that component for the surface but also by the ratio of the components. However, this simple and self-evident conclusion introduces serious difficulties in the analysis of the adsorption of mixtures if the analysis is attempted in the classical approach to the determination of the adsorption isotherms.

In the experimental method originally used to study adsorption from mixtures the concentration of the solution was assumed to remain constant, the only variable being the ratio of the dissolved components.[14] This method can give information on the preferential adsorption of the various polymers as a function of the presence of the other. However, it is not a strict method, since each change in the ratio of the components in solution produces a change in the thermodynamic quality of the 'mixed' solvent for each component, i.e. the adsorption conditions were not identical for mixtures of different composition.

There is also a second experimental method in which the concentration of one component only is varied in the solution of the mixture, whereas the concentration of the other component is kept constant. In this case we can construct the adsorption isotherm for the component of variable concentration. This experimental scheme is simply equivalent to studying the adsorption of the given component from solvents of different thermodynamic quality, and therefore it does not readily detect the specific aspects of the adsorption of mixtures if the system displays specific adsorption.

The third method (a continuous increase in the concentration of the solution, as in the classical method of constructing the isotherm) involves adding to the solution the two components in constant relative amounts. However, even this method cannot be called strict, as in this case we have a simultaneous adsorption of the two components in different proportions (depending on their relative adsorbability), and under these conditions each component is adsorbed from a solvent of thermodnamic quality appropriate for that component.

We know of no other method of studying the adsorption of mixtures of polymers. The most important aspect of the adsorption of a mixture of polymers is that it cannot be studied in the classical variant of the construction of adsorption isotherms: the specific features of the adsorption of mixtures are in fact determined by the difference and variability of the thermodynamic quality of the solvent for each component. Thus it is impossible to formulate a 'pure' experiment on the selectivity of the adsorption, since it is impossible to ensure that the solvent has the same thermodynamic quality for each of the polymers. The only way to design a 'pure' experiment is to examine the adsorption of the components from a melt of the two polymers, in the absence of a solvent. We have attempted a study of this type,[20] but even this was not a strictly adsorption-determined experiment.

If the discussion of the adsorption of mixtures is approached from the standpoint of dilute and semidilute solutions it becomes obvious that the aggregation and adsorption conditions should depend on the critical concentration for the overlapping of the macromolecular globules in the mixture, i.e. on the concentration region in which the contact and the overlapping of the globules of different polymers sets in. Obviously, under these conditions we cannot use the c^* values for the different components in the solvent, since in a solution of the mixture the thermodynamic quality of the 'mixed' solvent differs from the quality of the pure solvent and depends on the concentration and on the concentration ratio of the components.

II. Critical concentrations for solutions of polymer mixtures

The theory of solutions of mixed polymers from the point of view of their hydrodynamic properties is still not fully developed. Two approaches to the calculation of the critical concentrations in mixtures are possible.

Table 1. Critical concentrations of polymers in solutions of mixtures, determined by the expression $c^* = 1/[\eta]$.

A. PS–PBMA–CCl_4 system.			B. PC–PCL–$CHCl_3$ system		
c/g (100 ml)$^{-1}$ [a]	$[\eta]$/100 ml g^{-1}	c^*/g (100 ml)$^{-1}$	c/g (100 ml)$^{-1}$ [a]	$[\eta]$/100 ml g^{-1}	c^*/g (100 ml)$^{-1}$
PBMA–'mixed' solvent (PS–CCl_4)			PC–'mixed' solvent (PCL–$CHCl_3$)		
0	0.95	1.05	0	0.45	2.20
0.5	0.60	1.66	1.0	0.45	2.20
1.0	0.50	2.00	2.0	0.35	2.86
1.5	0.44	2.27	3.0	0.27	3.70
2.0	0.34	2.94	4.0	0.19	4.50
3.0	0.30	3.33	6.0	0.20	5.00
PS–'mixed' solvent (PBMA–CCl_4)			PCL–'mixed' solvent (PC–$CHCl_3$)		
0	1.10	0.90	0	0.090	11.1
0.25	0.90	1.11	0.5	0.075	13.3
0.50	0.80	1.25	1.0	0.065	15.4
1.00	0.75	1.33	1.5	0.050	20.0
1.50	0.50	2.00	2.0	0.045	22.0
2.00	0.40	2.50	2.5	0.040	25.0

Notes. The following symbols are used: PS polystyrene; PBMA polybutylmethacrylate; PC polycarbonate; PCL polycaprolactone.
[a] Concentration of mixed solvent.

The first uses well known relationships for determining c^*, but the characteristic viscosity of one of the components of the mixture is calculated in the presence of the second polymer, taken in a known proportion. We carried out these calculations for a series of polymer pairs, using their adsorption data given below. The critical concentration for the overlapping of the macromolecular globules was determined by the expression $c^* = 1/[\eta]$, where the characteristic viscosity was found by the standard method using an Ubbelohde viscometer. The special feature of the determination of the critical concentration in a polymer mixture in this approach is the use of a 'mixed' solvent. As can be seen from the data in Table 1 an increase in the concentration of the 'mixed' solvent produces a fall in $[\eta]$, and therefore also an increase in c^* for the given polymer. These data also show a worsening of the thermodynamic quality of the 'mixed' solvent (as compared with the pure solvent) for both the polymers in solution. Therefore the c^* values for the pure solvents cannot be used to study the adsorption of the components of a mixture in the concentration regions below and above the crossover. In all the three experimental methods of determining the adsorption considered above the component ratio in solution is not constant, and therefore the critical concentration of each of the components in the presence of the other determined in this way is also not constant. We consider this approach to be unacceptable also because the c^* values are determined without allowing for the fact that the bulk of the solution is filled with globules of two kinds, and that each kind is 'unaware' of the other. The region of uniform filling of the bulk by globules of two kinds will be in a different concentration region, defined by the size of the globules of each of the components and by their concentration in the solution.

Therefore we shall use an 'averaged' critical concentration for the mixture, determined from the 'averaged' characteristic viscosity. In contrast to the approach previously developed[21,22] we propose the following expression for the 'averaged' characteristic viscosity:

$$[\eta]_m = [\eta]_A\varphi_A + [\eta]_B\varphi_B \ , \qquad (1)$$

where φ_A and φ_B are the volume fractions of the components in their mixture, with $\varphi_A + \varphi_B = 1$.

Thus, for a mixture of the macromolecules A and B (and irrespectively of their thermodynamic compatibility) the crossover region should be reached by each of the polymers at concentrations below c_A^* or c_B^* because the bulk of the solution is already occupied by globules of molecules of kind A and B. We assume that $c_m^* = 1/[\eta]_m$. In that case the averaged crossover concentration is a function of the concentration ratio of dissolved molecules of kinds A and B.

The critical concentrations and the characteristic viscosities for a range of pairs and for their constituent components in a common solvent are shown in Tables 2 and 3. We have studied the adsorption of these same pairs. The PS–PBMA and PS–polydimethylsiloxane (PDMS) system are thermodynamically incompatible in solution, whereas the PC–PCL pair is compatible in the solvents which we have chosen.

An analysis of the data in Tables 2 and 3 shows that in the PS–PBMA system with similar c^* values for the two components

Table 2. Critical concentration and critical viscosity in the polymer–solvent system.

System	$[\eta]$/100 ml g^{-1}	c^*/g (100 ml)$^{-1}$
PS–CCl_4	1.13	0.88
PBMA–CCl_4	0.96	1.04
PCL–$CHCl_3$	0.09	11.10
PC–$CHCl_3$	0.45	2.20
PC–$CH_3COOC_2H_5$	0.46	2.20
PDMS–$CH_3COOC_2H_5$	0.11	9.00

Table 3. Characteristic viscosities of the mixture $[\eta]$ (in 100 ml g^{-1}) and critical concentrations [in g (100 ml)$^{-1}$] of polymers in solutions of mixtures determined from the 'averaged' characteristic viscosity.

c_A^*	$[\eta]_m$	c_m^*	c_B^*	c_A^*	$[\eta]_m$	c_m^*	c_B^*
PS–PBMA–CCl_4 system							
0.5	0.99	1.01	2.5	2.0	1.07	0.93	1.0
1.0	1.02	0.98	2.0	2.5	1.10	0.90	0.5
1.5	1.05	0.95	1.5				
PCL–PC–$CHCl_3$ system							
1.0	0.41	2.4	9.0	6.0	0.22	4.5	4.0
2.0	0.38	2.7	8.0	7.0	0.19	5.3	3.0
3.0	0.34	2.9	7.0	8.0	0.16	6.2	2.0
4.0	0.31	3.2	6.0	9.0	0.13	7.7	1.0
5.0	0.27	3.7	5.0				
PS–PDMS–$CH_3COOC_2H_5$ system							
0.5	0.28	3.6	0.5	2.0	0.34	2.9	1.0
1.0	0.34	2.9	0.5	2.5	0.35	2.8	1.0
1.5	0.37	2.7	0.5	0.5	0.13	7.7	9.0
2.0	0.38	2.6	0.5	1.0	0.14	7.1	9.0
2.5	0.40	2.5	0.5	1.5	0.155	6.45	9.0
0.5	0.22	4.5	1.0	2.0	0.17	5.9	9.0
1.0	0.28	3.6	1.0	2.5	0.18	5.5	9.0
1.5	0.31	3.2	1.0				
PDMS–PS–$CH_3COOC_2H_5$ system							
2.0	0.175	5.7	0.5	14.0	0.132	7.6	1.0
6.0	0.13	7.5	0.5	18.0	0.130	7.8	1.0
10.0	0.125	7.9	0.5	2.0	0.30	3.4	2.5
14.0	0.12	8.3	0.5	6.0	0.21	4.8	2.5
18.0	0.119	8.4	0.5	10.0	0.18	5.7	2.5
2.0	0.220	4.5	1.0	14.0	0.16	6.2	2.5
6.0	0.160	6.4	1.0	18.0	0.15	6.7	2.5
10.0	0.139	7.2	1.0				

the parameter c_m^* is weakly dependent on the ratio of the components in solution. On the other hand for the PC–PCL system we observe a marked increase in c_m^* with increasing concentration of PCL, due mainly to the only moderately high molecular mass of PCL. In the PS–PDMS system with constant (but different) concentrations of PDMS the critical concentration of the mixture falls with increasing concentration of PS, but with a constant concentration of PS and a variable concentration of PDMS it increases. These results must be included in any analysis of the adsorption from mixtures in dilute and semidilute solutions.

III. Adsorption from solutions of mixtures

The experimental methods of determining the adsorption from mixtures used in our work have already been described.[18,19] In this section we present data on the adsorption on Aerosil of three pairs of polymers: PS–PBMA and PS–PDMS (incompatible in solution) and PC–PCL (compatible). The adsorption of PS–PBMA and PCL–PC mixtures was studied at constant concentrations of the mixture in solution and different component ratios, and the adsorption in the PS–PDMS system was studied at a constant concentration of one of the components and a variable concentration of the other.

1. The polydimethylsiloxane – polystyrene – ethyl acetate system

The dependence of the adsorption of PDMS from a mixture with PS in a common solvent at different constant concentrations of PS (above and below the c^* value for PS) is shown in Fig. 1 in A (adsorption) – c/c_m^* coordinates. As can be seen, in the crossover region and above c_m^* the adsorption decreases after going through a maximum, both in the adsorption of pure PDMS and in the adsorption from its mixtures containing different amounts of PS.

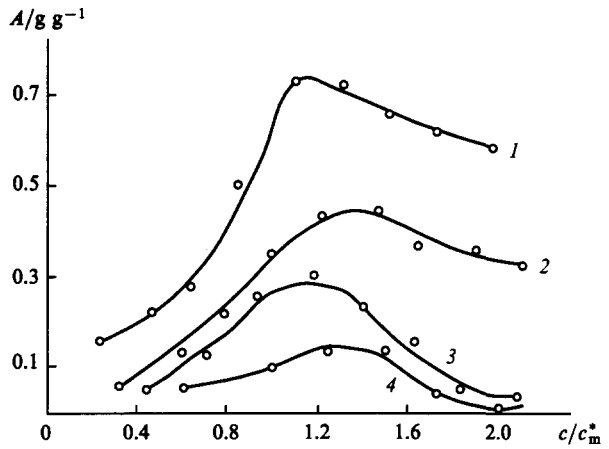


Figure 1. Dependence of the adsorption of PDMS from an individual solution (*1*) and from its mixtures with PS (*2–4*) in ethyl acetate on the concentration of PDMS for PS concentrations of 0.5 (*2*), 1.0 (*3*), and 2.5 (*4*) g(100 ml)$^{-1}$.

The absolute adsorption values are very large, suggesting aggregative adsorption. The same suggestion applies also to the decrease in adsorption at concentrations above c^*_m. As the concentration of PS in the solution is increased (thus worsening the thermodynamic quality of the 'mixed' solvent) the adsorption decreases but the maximum in the region of reduced concentrations greater than 1 is retained (above the crossover region). As has already been mentioned we ascribe this behaviour to the worsening of the quality of the solvent for PDMS, which by decreasing the size of the globules also decreases the size of the aggregates.

In Fig. 2 we show the corresponding data for PS, which indicate that in this case the effects discussed above are less marked (even though the aggregation of PS should be much greater because of its greater molecular mass, see below). The adsorption of PS is much lower, and almost independent of the concentration of PDMS, but an adsorption maximum is observed in the region of concentrations much lower than c^*_m. Obviously, in this case PDMS has a higher affinity for the adsorbent surface, and this produces a higher selectivity of the adsorption, promoted by noncompatibility with the PS.

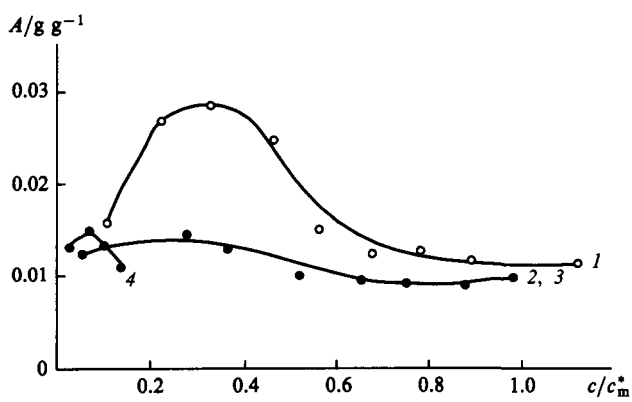


Figure 2. Dependence of the adsorption of PS from an individual solution (*1*) and from its mixtures with PDMS (*2–4*) in ethyl acetate on the concentration of PS for PDMS concentrations of 0.5 (*2*), 1.0 (*3*), and 9.0 (*4*) g (100 ml)$^{-1}$.

2. The polystyrene – polybutylmethacrylate – carbon tetrachloride system

The plots in Fig. 3 show that in the crossover region the adsorption of PS from a mixture with PBMA forms a broad maximum, whereas the adsorption of PBMA increases monotonically (Fig. 4). Under these conditions the adsorption of PS from the mixture is lower, and that of PBMA is higher than for the same adsorptions from a pure solvent. These results denote preferential adsorption from the mixture with PBMA. Evidently, in this case the noncompatibility of the components promotes the preferential adsorptions of one of the components under conditions in which the adsorption of the pure components from the common solvent are approximately equal.

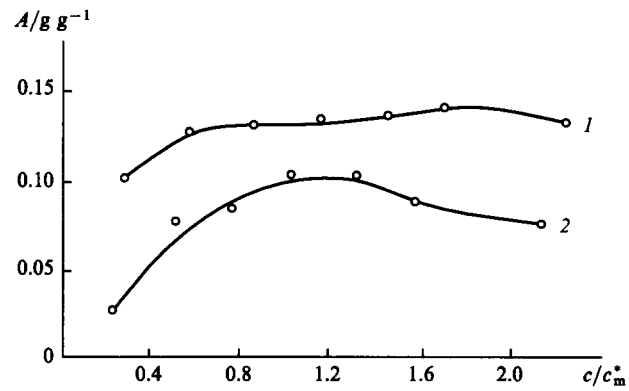


Figure 3. Dependence of the adsorption of PS from an individual solution (*1*) and of its mixture with PBMA (*2*) in carbon tetrachloride on the concentration of PS.

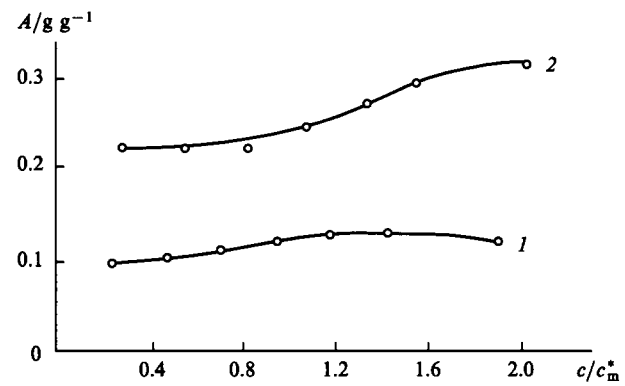


Figure 4. Dependence of the adsorption of PBMA from an individual solution (*1*) and from its mixture with PS (*2*) in carbon tetrachloride on the concentration of PBMA.

In Fig. 5 the data for this system are presented differently: in the form of a plot of the ratio of the adsorptions of the components against the concentration of the mixed solvent (the concentration of PBMA in solution is plotted horizontally) while keeping the overall concentration of the solution constant at 3 g (100 ml)$^{-1}$. It is clear from this figure that the PBMA is adsorbed preferentially at all component ratios in the solution. However, a minimum is found in the plot. A similar minimum occurs (Fig. 6) in the plot (obtained in our laboratory) of the second virial coefficient A_2 for the ternary PS – PBMA – solvent system. The concentration at which the minimum for this pair of polymers is seen coincides with the c^* value of each of the components (we note that these are not very different) and with c^*_m. After passing through c^*_m the ratio of the adsorptions increases again.

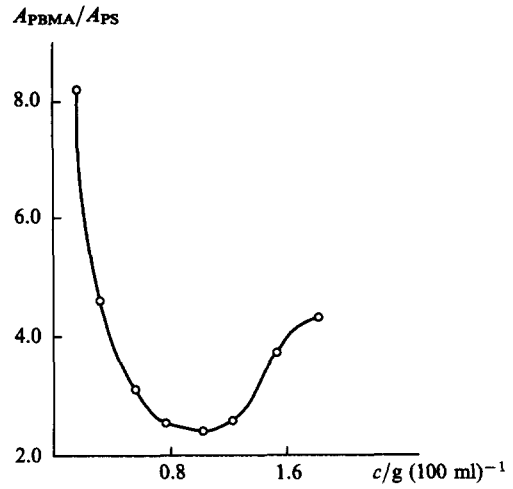


Figure 5. Dependence of the ratio of the adsorptions of PBMA and PS on the concentration of PBMA.

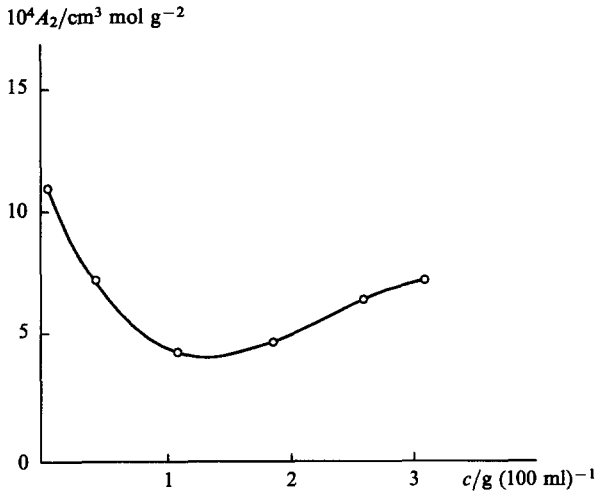


Figure 6. Dependence of the second virial coefficient A_2 on the concentration of the 'mixed' solvent for the PS–'mixed' solvent (PBMA–CCl_4) system.

Comparing Figs 5 and 6 shows the important role of the varying thermodynamic quality of the 'mixed' solvent in the adsorption from mixtures.

3. The polycaprolactone – polycarbonate – chloroform system

The adsorption of a compatible pair of polymers (polycaprolactone and polycarbonate) in a common solvent has been studied from a solution of constant concentration but variable composition. The dependence of the adsorption of PCL on c/c_m^* is shown in Fig. 7. For PCL we see a maximum in the crossover region. The adsorption of PCL is clearly predominant, in spite of its low molecular mass, and therefore the adsorption of PC begins only at high enough concentrations of this polymer in the mixture (Fig. 8), exceeding c^*. However, the adsorption of each of the components from the common solvent is higher than from the mixture: we attribute this effect to the thermodynamic compatibility of the components.

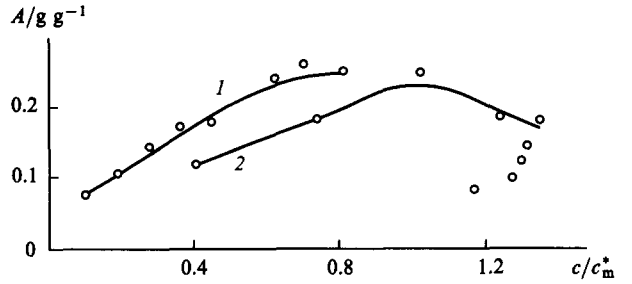


Figure 7. Dependence of the adsorption of PCL from an individual solution (*1*) and from its mixture with PS (*2*) in chloroform on the concentration of PCL.

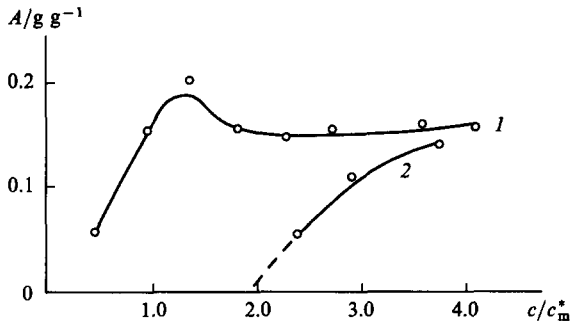


Figure 8. Dependence of the adsorption of PC from an individual solution (*1*) and from its mixture with PCL (*2*) in chloroform on the concentration of PC.

IV. Aggregation in solutions of macromolecules and in their mixtures

We shall now examine some experimental results on the formation of aggregates of these polymers in solution. In order to facilitate the comparison with the data on the adsorption of polymers discussed above these results were obtained by the turbidity spectrum method, which allows the size and number of aggregates to be determined from the spectral dependence of the intensity of light scattering in the visible region. The theoretical foundations of this method were laid by Heler and Pangonic[23] on the basis of the theory of Mie,[24] developed for isotropic spheres. We used a modification of this method.[25]

Data on the formation of aggregates in solutions of PS, PBMA, and PC are shown in Table 4 (see next page). Solutions of PDMS are transparent in the visible region of the spectrum. Aggregates of low-molcular PCL were also not detected, probably because of their small size (the turbidity spectrum method can be used to determine the size of aggregates above 200 Å).

An analysis of the results in Table 4 shows that in this polymer the formation of aggregates begins at concentrations below c^*, and also in the region above crossover. The size of the macromolecular aggregates usually increases with the concentration and depends on the temperature (but the temperature dependence of the adsorption has not been studied yet). However, the dependences on concentration and temperature are not unambiguous, because the quantities of interest are determined both by the change in the quality of the solvent with temperature and by the equilibrium constant of the reaction between aggregated and nonaggregated macromolecules, which is also temperature dependent. In different systems the size and number of the aggregates vary with temperature in different ways in the regions above and below c^*, and therefore it is difficult to identify any well defined trends in their changes.

Table 4. Size r (in Å) and number of macromolecular aggregates per unit volume N (in 10^{-9} cm^{-3}) as a function of the concentration of solution c [in g $(100\ ml)^{-1}$] at 25 °C.

c	r	N	c	r	N
PS–CCl_4					
0.5	400	2.3	2.5	620	2.0
1.0	460	5.6	3.0	700	1.6
1.5	530	4.2	3.5	1400	0.1
2.0	590	2.6			
PBMA–CCl_4					
0.5	400	4.50	2.5	1900	0.08
1.0	700	1.30	3.0	2700	0.07
1.5	900	0.48	3.5	3300	0.01
2.0	1400	0.20			
PC–$CHCl_3$					
1.0	300	0.9	6.0	600	34.7
2.0	400	3.2	7.0	600	37.0
3.0	500	5.0	8.0	700	53.0
4.0	450	18.8	9.0	700	80.0
5.0	500	25.5	10.0	800	90.0
PS–$CH_3COOC_2H_5$					
0.25	1000	0.017	3.00	890	5.90
0.50	2000	0.08	5.00	890	6.88
1.00	3000	0.10	7.00	890	7.14
1.50	4000	0.27	8.00	900	7.64
2.00	800	4.40	10.00	890	7.90
2.50	850	5.04	12.00	700	9.80

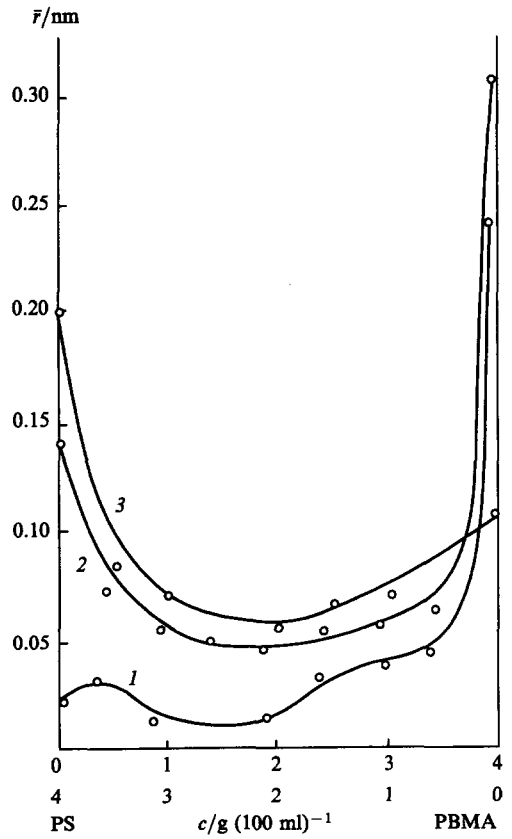


Figure 9. Dependence of the average size of the aggregates of macromolecules in a PS–PBMA–CCl_4 mixture on the composition of the 'mixed' solvent. T, °C: (*1*) 10; (*2*) 25; (*3*) 60.

However, it is obvious that aggregation processes take place also in solutions of mixtures, and that the trend towards aggregation of the molecules of each kind should be most marked when the thermodynamic compatibility of the components is low and the thermodynamic quality of the 'mixed' solvent is poor. In Fig. 9 we also show the averaged size of the aggregates of macromolecules in a PS–PBMA mixture as a function of the composition of the 'mixed' solvent [for an overall solution concentration of 3 g $(100\ ml)^{-1}$]. As can be seen the presence of a 'second' polymer (incompatible with the 'first') leads to a marked decrease in the size of the aggregates as a result of the worsening of the thermodynamic quality of the solvent and of the possible collapse of the macromolecules.[26] This is consistent with the data on the characteristic viscosity of one of the components in the presence of the other. The decrease in size of the macromolecules may lead to a decrease in the average size of the aggregates in a solution of the mixture.

V. Conclusion

The experimental data quoted above show the existence of an interdependence between the adsorption of polymers from a mixture, the thermodynamic compatibility of the components in solution, the change in the thermodynamic quality of the 'mixed' solvent, and the critical crossover concentration for each component (on the one hand) and the mean critical concentration for the mixture. The influence of the aggregation of macromolecules in solutions of mixtures of polymers produced by the above factors on the adsorption in the concentration regions above and below c_m^* is also obvious. As a rule the adsorption decreases as the system goes through c_m^*: this may be due (among other reasons) to the fact that the size and number of the macromolecular aggregates which constitute the mixture of components also depend on c^* and are not identical in the regions below and above c^*. Since the formation of aggregates produces a change in the thermodynamic quality of the solvent it is obvious that the presence of a second component must alter the formation conditions of the aggregates by worsening the thermodynamic quality of the 'mixed' solvent (irrespectively of whether the given pair of polymers is compatible in solution).

The high adsorptions of both the individual components and their mixture can be explained only in terms of the aggregative adsorption mechanism: differences in the behaviour of the systems during adsorption in the region above or below the crossover can be attributed to changes in the aggregation conditions of macromolecules of different kind and different concentration regimes under conditions of continuously varying thermodynamic quality of the solvent. The passage through the crossover region produces changes in the structure of the solution as a result of the formation of a network of contacts and of the overlapping of the macromolecular globules. However, in reduced coordinates the passage through the crossover region often does not lead to significant changes in adsorption, i.e. the adsorption is not markedly affected by whether the system is close to or far from the crossover. Therefore the influence of regime of the mixed solution on the adsorption of its components can probably be identified from the dependence of A on c/c_m^*.

Thus the change in the thermodynamic quality of the solvent produced by the introduction of various quantities of a second polymer is mainly responsible for the behaviour of the adsorption from mixtures and for the selectivity of the adsorption of one of the components. Another factor which lack of space prevented us from discussing in the present review is the affinity of the components towards the adsorbent surface. This requires studies on different adsorbents. The simultaneous influence of various factors has so far prevented the development of a theory of adsorption from mixtures.

The theory of adsorption from mixtures is still in its first stage of development, in spite of the fact that the first papers on this topic were published 17 years ago. The number of

experimental data is small, and the number of variables to which the adsorption is sensitive is large: they include the molecular mass of the components,[27] the nature of the adsorbent,[29] and the interaction of the components in solution (the thermodynamic interaction parameter), and also the molecular mass distribution, the formation of aggregates in different regimes, the problems associated with their determination, etc.

However, since the structure of the adsorption layers of mixtures is determined by the conditions of adsorption from the mixtures, and since the adsorption layers play an important role in polymeric composite materials based on multicomponent polymer systems, the further study of the adsorption of mixtures and also the study of the structure of adsorption layers of mixtures[30] are of the greatest importance.

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