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COMPARATIVE ANALYSIS OF THE MODIFYING EFFECT OF INDIVIDUAL POLYELECTROLYTES AND THEIR COMPLEXES WITH SURFACE-ACTIVE SUBSTANCES

Kainzhamal I. Omarova, Moldir Zh. Kerimkulova

Al-Farabi Kazakh National University
71 Al-Farabi str., 050040, Almaty, Republic of Kazakhstan
E-mail: omar_kainzhamal@mail.ru

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ABSTRACT

The results of contact interaction of hydrophobic particles, wetting angles of solid surfaces modified by polyelectrolytes and polycomplexes and the part of a surface taken by macromolecules and polycomplexes on adsorption layer were analyzed. The determinative role of the polycomplex compacting degree on their modifying effect was shown.

Keywords: polyelectrolyte, surfactants, modification, hydrophobic particles, contact interactions, modifying effect, associates.

INTRODUCTION

Polyelectrolytes (PE) depending on the character of interaction of macromolecules each other and with the solvent molecules and on the concentration of the solution, can coexist either in the form of flexible chain (statistical coils) or as dense globules of coiled chains, as well as associates with each other. The composition and pH of the medium determine the charge of PE macromolecules thus affecting the degree of intra- and intermolecular association. For synthetic polyelectrolytes (SPE) such as polyacrylic acid (PAA), polymethacrylic acid (PMAA), poly-2-methyl-5-vinylpyridine (PMVP) the tendency to form aggregates and globules of macromolecules is quite pronounced in the concentration range of 10^{-2} %. The mentioned range of concentrations is called the concentration of conformational conversion (CCC) [1].

In diluted solutions of PE (C < CCC), the intramolecular interactions are weakened, thus creating conditions for definite orientation of macromolecules in the adsorption layer depending on the nature of the solid surface. On quartz surface the adsorption is mainly determined by the electrostatic interaction of the functional groups of PE macromolecules with opposite charged centers of SiO_2 contributed by the heterogeneous charge of the quartz surface (the presence of SiO^- - and $SiOH_2^+$ groups). The number of the charged groups depends on pH of the contacting medium. In solutions of polyacids, the number of $SiOH^+_2$ groups increases with the decrease in pH at the increase of polyacid (PAA, PMAA) solutions concentration. The same ratio between pH and the number of active groups is also preserved in solutions of polybases – polyethyleneimine (PEI): the increase in pH and, correspondingly, groups of SiO^- with the increase of polybase solutions concentration. The adsorption of macromolecules on the low energy surface of Teflon proceeds due to the hydrophobic interaction of nonpolar radicals of PE and the surface of Teflon.

In the range of low concentrations of PE solutions, the individual macromolecules are able to uncoil on the surface of the adsorbent under the action of adsorption forces and to be oriented by the corresponding groups to the aqueous phase: on quartz - by hydrophobic groups (hydrophobization of SiO_2), on Teflon - by polar ones (hydrophilization of Teflon). The hydrophobic and hydrophilic action of polyelectrolytes appropriately increases with the increase of the molecular mass and the hydrophobicity of the macromolecules [2, 3]. The mentioned factors enhance the adsorption ability of macromolecules on nonporous adsorbents, the examples of which are both quartz and Teflon. Functional groups of PE take part in interaction with the quartz surface. In case of Teflon surface nonpolar radicals take part in the interaction.

The modifying action of SPE increases with introduction of low molecular surface active substances (SAS) into solution [4, 5]. The electrostatic interaction of opposite charged SAS and the formation of hydrogen bonds in case of nonionic SAS with macromolecules of PE is accompanied by a blockage of polar groups of PE and hydrophobization of the macromolecular chain. Such decrease in the number of the free functional groups should lead to reduction of the modifying effect. However, for associates SPE-SAS, the determining factor is likely to be compacting of macromolecules when interacting with SAS.

It can be supposed that globulization of macromolecules will be accompanied by the increase in the number of polar groups per unit length of macromolecules, or more clear, on the unit surface of SPE-SAS complex particle. The number of polar groups determines the adsorption of PE, their associates on the surface of quartz and the degree of hydrophilization of Teflon surface [4, 5].

The aim of this study is the investigation of the modifying effect of individual polyelectrolytes and their complexes with surface-active substances on the wetting ability of hydrophilic (quartz) and hydrophobic (Teflon) solid surface.

EXPERIMENTAL

The analysis of data on the forces of contact interactions of solid particles in solutions of PE and their mixtures with SAS verifies the suppositions. The experimental study on the interaction of two solid surfaces is of interest for solving the problems of stability of disperse systems that can be controlled with the help of SAS and polymers. The problem of stability concerns mainly highly dispersed hydrophobic systems, for example, hydrophobized glass balls. The hydrophobization of balls with diameters of 1 mm was carried out by holding them in 5 % benzene solution of trimethylchlorosilane for 5 hours. To control the degree of surface hydrophobization, glass and quartz plates were placed simultaneously in the same solution and after drying the angle of water wetting (θ) was measured. For different plates, the value of θ was 105 - 112^0 corresponding to the angle of water wetting of nonpolar clean surfaces (Teflon, paraffin). Therefore, joint consideration of the results on the modification of Teflon PE and SAS with the data on contact interaction of methylated particles in the presence of the same components is possible. Wetting angle θ was determined using horizontal microscope through drawing a tangent to water drop surface.

The methodology for identification of the adhesion forces between hydrophobic balls is based on the usage of magnetic-electrical system of type M-122 galvanometer [6]. One ball is glued to galvanometer arrow; another ball is glued to reitor manipulator. The balls are adjoined in the absence of current and an adhesion force (f) is created by putting through current of certain value during certain time. Then a current of opposite direction is applied to separate the balls. The power of separation is equal to the adhesion force.

RESULTS AND DISCUSSION

The increase in particles interaction at low concentrations of PE solution and the formation of a plateau in the range of 10^{-5} - 10^{-4} base-mole/l for the studied synthetic polyelectrolytes (PAA, PMAA, PEI) are identified [7].

In the given range of concentration the value of wetting angles of Teflon, modified by polyelectrolyte, shows weak hydrophilizing effect of polyelectrolyte. The wetting angles are 2 - 5^o smaller than those for clean surface of Teflon. The mentioned fact must lead to at least insignificant weakening of cohesive force between methylated glass balls. The observed increase in contact interaction is likely to be related to “bridge formation” between particles from adsorbed macromolecules which, according to the opinion of most researchers, is the cause of the flocculating action of polymers at low concentration in solution.

The increasing additives of PE sharply reduce the cohesive forces. This results in a noticeable reduction of wetting angles of Teflon (88 - 91^o). This regularity agrees with the common, experimentally verified conception of the stabilizing action of polymers at their definite concentration in the system. The hydrophilization of the particles during adsorption of water soluble poly-

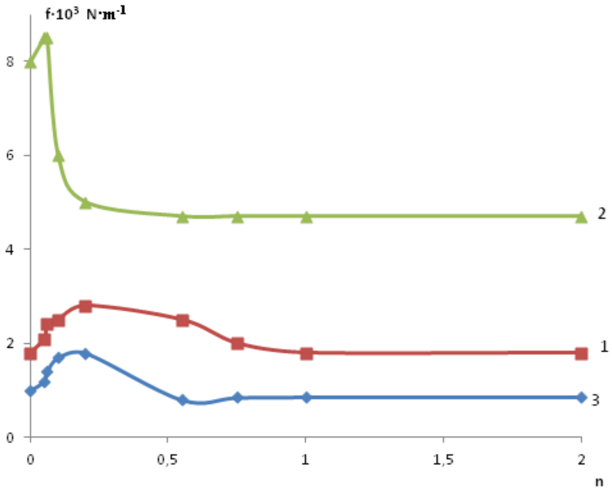

Fig. 1. The effect of additives of SAS to solutions of polyacids on the cohesive force of hydrophobic balls: 1-OP-7; 2-PMAA (M_η=1·10^5 c=0.01 M); 3-OP-7/PMAA.

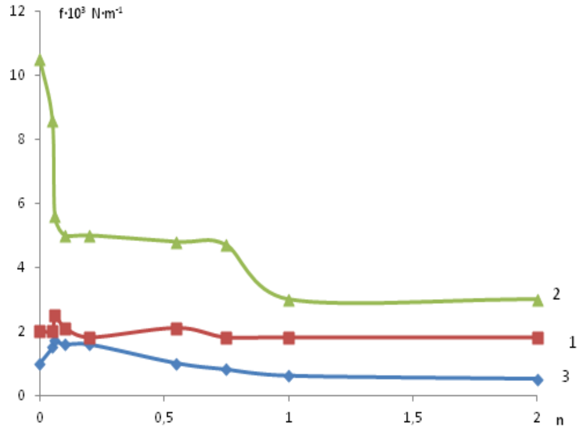

Fig. 2. The effect of additives of SAS to the solutions of polyethyleneimine on the cohesive force of hydrophobic balls: 1-OP-7; 2-PEI (M_η=1·10^3, c=0.01 M); 3-OP-7/PEI.

mers, in particular polyelectrolytes, containing a large number of hydrophilic groups, lead to the appearance and strengthening of the salvation factor of stability. The salvation of the disperse phase is considered also to be a dominating factor during the stabilization of hydrophobic particles hydrophilized by the adsorption layers of low molecular SAS [7].

In the mixtures of ionic SAS and PE solutions, independently on the nature of polyelectrolytes and SAS, one can observe reduction of cohesion forces between methylated balls in comparison with those for individual SAS and PE [7]. In the mixtures of PAA and cetyltrimethylammonium bromide (CTAB), the minimal values of cohesive forces correspond to the minimal wetting angles of Teflon (72 - 80^o). This confirms the fact that the presence of polar groups of both SPE and SAS in associates PAA-CTAB impart them greater hydrophilicity in relation to methylated particles (including Teflon). Thus, the change in wettability of the surface of nonpolar particles exerts a significant effect on the contact interaction of dispersed particles.

In the mixtures of SPE-nonionic SAS solutions, the dependence of the cohesive forces (f) and the wetting angles (θ) of hydrophobic surfaces on the relative concentration of SAS (n, n = V_{SAS}/V_{PE}, V_{PE} - const) in the mixture is practically of the same form. In the system OP-7/PMAA (OP-7-oxyethylated alkylphenol), an insignificant increase of θ in the range of small n [5] also leads to a slight growth of cohesive forces with further decrease and formation of a plateau with increasing of n in accordance with the change of wetting angles (Fig. 1). In the mixtures OP/PEI, one can also observe correlation between the course of the curves θ vs. n and f vs. n (Fig. 2). Though, as mentioned above, the interaction of SPE and SAS is accompanied by hydrophobization of the polyelectrolyte macromolecule. OP-7/PMAA and OP/PEI were studied simultaneously during one - two months. The macromolecules of PMAA are negatively charged while the macromolecules of PEI are positively charged.

Apparently, the counteracting effect of hydrophobization of macromolecules is compacting of the macromolecule coil as a result of enhancement of hydrophobic interactions leading to “liberation” of polar hydrophilic groups on the surface of the complex. The compacting of the coil increases adsorption of the complex on the unit area of solid bodies’ surface. In [8] the authors showed that the value of the limiting adsorption of α-chymotrypsin complex with sodium oleate (OlNa) on Teflon exceeds twice that of α-chymotrypsin on the same adsorbent. Such increase in adsorption of the complex is related to the three times decrease in the area occupied by the complex of α-chymotrypsin with OlNa on the surface of the adsorbent compared to the area occupied by a free macromolecule.

To confirm such assumption about the regularities of the modifying effect of individual synthetic polyelectrolytes and polycomplexes of SAS, the theory of wetting of heterogeneous surfaces [9] was used. This theory is based on the provision for the heterogeneity of individual parts of practically most solid surfaces. So, on the quartz surface, there are both negatively and positively charged and no ionized parts, the ratio of which depends on pH of the contacting liquid. Specific surface energies of solids at the interface of the liquid medium are the result of contributions of all parts. For example, for the surface containing different parts (type 1 and type 2) it is:

$$\sigma_m=x\sigma_{S1}+(1-x)\sigma_{S2} \tag{1}$$

where x is the relative share of the area occupied by the parts of the type 1 on the whole surface; σ_{S1} and σ_{S2} are surface tensions of homogeneous parts of the type 1 and 2 at the interface with the medium (for example, gas).

At a contact of a solid surface with a liquid, a similar equation can be written:

$$\sigma_{SL}= x\sigma_{S1L} + (1-x)\sigma_{S2L} \tag{2}$$

Taking into account the fact that an equilibrium form of the liquid drop on the surface of solid is determined by Young's equation

$$\sigma_S - \sigma_{SL} = \sigma_{SL} \cos\theta \tag{3}$$

and taking into account equation (2) it is:

$$\cos\theta = x\cos\theta_1 + (1-x) \cos\theta_2 \tag{4}$$

where θ_1 and θ_2 are the angles of wetting of homogeneous parts 1 and 2 by this liquid.

When modifying solids with polyelectrolytes, on the surface exist parts covered and uncovered with the adsorbed polymer. The parts covered with the adsorbed layer of macromolecules can be heterogeneous as the composition of SPE macromolecule includes both hydrophilic and hydrophobic groups. It can be assumed that all hydrophobic groups of macromolecules are wetted with water similarly and the wetting angle is the same as that of water on Teflon (paraffin, $\theta_2=110^o$). At the same time, the polar groups in the composition of macromolecules are wetted with water similarly and the wetting angle is the same as that on the surface of quartz ($\theta_1 = 0^o$). At such quite probable assumptions, equation (4) allows to evaluate quantitatively the share of hydrophilic (x) and hydrophobic (y = 1 - x) parts on the surface according to the angles of wetting modified quartz (Teflon) with water, thus calculating the share (β) of the surface covered with adsorbed links of macromolecules.

Tables 1 and 2 present the values of β calculated for individual polyelectrolytes and their associates with SAS. The value of β naturally increases with the increase in concentration (up to CCC), molecular mass and hydrophobicity of macromolecules (Table 1).

It should be noted that the share of hydrophobized parts on quartz and hydrophilized parts on Teflon is not great (maximum 17 and 27 %, respectively), i.e. a rare feed adsorption layer is formed on the surface. This result shows that on the surface of quartz and Teflon there are only those molecules whose maximum number of links contact directly with the surface.

The share of hydrophilisized parts on Teflon is higher than that of hydrophobized parts on quartz that shows a significant contribution of hydrophobic interactions to

Table 1. The share (%) of quartz and Teflon surface parts, occupied by adsorbed polyelectrolyte macromolecules.

PE c, %	PAA $M_\eta = 1.7 \cdot 10^4$		PAA $M_\eta = 1.8 \cdot 10^5$		PMAA $M_\eta = 1.8 \cdot 10^5$		PMVP $M_\eta = 1.9 \cdot 10^4$	
	quartz	Teflon	quartz	Teflon	quartz	Teflon	quartz	Teflon
$1 \cdot 10^{-5}$	0.7	0.7	1.5	0.7	2.0	0.7	6.0	0.7
$1 \cdot 10^{-4}$	0.9	2.2	2.6	4.4	3.3	4.4	7.7	4.4
$1 \cdot 10^{-3}$	2.0	8.0	4.6	10.2	5.5	15.3	10.2	16.8
$1 \cdot 10^{-2}$	3.7	14.6	7.7	20.4	9.0	24.4	13.0	27.0
$1 \cdot 10^{-2}$	-	-	-	-	-	-	17.0	-
$1 \cdot 10^{-1}$	1.1	10.6	1.1	10.6	1.1	10.6	0.2	11.7
1.0	0.2	2.2	0.2	2.2	0.2	2.2	0.2	2.2

Table 2. The share (%) of either quartz or Teflon surface parts occupied by adsorbed associates SPE-SAS.

SPE+SAS $n = \frac{[SAS]}{[PE]}$	PAA+CTAB $M_\eta=1.9\cdot10^4$		PAA+CTAB $M_\eta=1.0\cdot10^6$		PMVP+CTAB $M_\eta=1.0\cdot10^6$		PMVP+DDS* $M_\eta=1.9\cdot10^5$		PMVP+DDS $M_\eta=3.4\cdot10^5$	
	quartz	Teflon	quartz	Teflon	quartz	Teflon	quartz	Teflon	quartz	Teflon
0	1.7	-	1.7	-	1.7	-	0.1	-	0.1	-
0,1	-	51.9	-	50.3	17.8	54.3	2.3	-	9.5	-
0,2	13.0	33.9	25.2	48.3	29.3	51.9	7.6	6.9	17.8	13.0
0,4	-	-	-	-	-	-	15.3	25.4	29.3	20.6
0,5	13.8	21.9	24.2	35.9	27.2	40.9	-	-	-	-
0,8	-	15.6	-	27.0	-	32.1	26.4	37.2	42.8	43.4
1,0	11.7	13.0	19.6	23.2	24.2	28.3	28.3	20.6	45.3	28.2
1,5	8.9	8.1	13.8	15.6	19.6	19.4	24.3	9.4	39.3	8.1
2,0	5.6	6.9	7.1	13.1	16.2	15.6	15.3	5.7	28.3	5.7

**DDS-natrium dodecylsulphate*

the adsorption of polyelectrolytes on Teflon. According to [8], on the surface of hydrophobic adsorbents, the degree of uncoiling of protein molecules is higher than that on the surface of hydrophilic materials. According to this fact, during adsorption of SPE on Teflon takes place the increase in the area occupied by one macromolecule on the surface and the number of polar groups oriented to the aqueous phase.

The analysis of the data presented in Tables 1 and 2 shows a considerable increase, both on quartz and Teflon, in the share of the area occupied by polyelectrolyte complexes of SAS in comparison with those for individual PE. This difference is especially pronounced for Teflon. So, on the surface of quartz modified with PAA with $M_\eta = 1.7\cdot10^4$, x_{max} is 3.7 %, and when modifying with PAA-CTAB, x_{max} is 13 % ($\Delta_x = 9.5$). In case of Teflon – for PAA y_{max} is 14.6 %, for complexes PAA-CTAB y_{max} is 35.9 % ($\Delta_y = 21.3$). Such divergence is observed for all PE and their complexes with the corresponding SAS. This difference in the values of x_{max} and y_{max} for individual PE and complexes PE-SAS appropriately increases with the increase in the molecular mass and intensification of the complex formation process between SPE and SAS and compacting of macromolecules.

Thus, interaction of synthetic polyelectrolytes with micelle forming surface active substances – weak polymer acids with cationic SAS and polymer bases with anionic SAS is accompanied by the increase in hydrophobicity of polymer chains and further significant compacting of polymer coils is determining during modification of solid surfaces. The compacting of polymer coils increases the share of the surface occupied by the adsorbed polymer. The presence of SAS molecules in the complex SPE-SAS imparts the latter the greater polarity in relation to extremely hydrophobic surfaces (paraffin, Teflon). The lyophilizing action of SAS is developed at a definite ratio of SAS/PE and is especially noticeable during formation of complexes PE-nonionic SAS. In our experiments, without addition of SAS, the concentration of polyelectrolyte exceeds the concentration conformational conversion (0.01 %) and does not render a modifying effect. The introduction of SAS allows increasing by nearly one decimal order the concentration of polyelectrolyte at which PE can modify the surface of solid. In case of adding nonionic SAS at $n > 5$, the polyelectrolyte complex of SAS is a macromolecule "entangled" with micelles of SAS which decreases during adsorption the wetting angle of Teflon to 20^o and the share of hydrophilized parts on the surface of Teflon x is 78 %.

The products of interaction of PE and SAS are new high molecular surface active substances. The possibility of controlling the surface hydrophile-lipophile balance, electrostatic free energy and conformation of SPE macromolecules using SAS of different nature opens the prospects of fine adjustment of their modifying action on solid surfaces. The peculiarity of this approach is simplicity of its realization without an additional complex instrumentation, low consumption of both polyelectrolytes and SAS. In practical terms, mixtures SPE-SAS are of interest for plastification and hardening of concrete mixes and especially their use in case of low active binders presented by electrothermophosphoric, blast-furnace, ash and slag wastes of thermal power plant. Development of the scientific bases of this direction would allow realizing wasteless production.

It is necessary to carry out investigations on the regularities of modification with polycomplexes of capillary-porous systems, in particular, membranes with the aim to increase their electrochemical activity and optimization of membrane methods for demineralization of natural and sewage waters - a progressive tendency in the development of demineralization technology [10].

Thus, the fields of practical application of adsorption modification of solid surfaces with synthetic polyelectrolytes and polycomplexes are numerous and further intensive scientific investigations are necessary.

CONCLUSIONS

Share of solid surface covered by adsorbed segments of individual SPE macromolecules and their associates with SAS is calculated based on wetting theory of heterogeneous surfaces. The increase of surface share occupied by mixtures of SPE and SAS (max 33 - 48 % of surface on Teflon and 13 - 29 % on surface of quartz) was identified. Associates of SAS keep compact structure during adsorption on quarts. They are loosened on surface of Teflon due to strong hydrophobic interaction of no polar radicals of PE with Teflon.

The modifying effect of associates of SPE and nonionic SAS depends on the concentration of SAS in a mixture. Strongly hydrophylized associates of SPE and SAS micelle are formed in fields where concentration of nonionic SAS is greater than critical concentration of micelle formation. Adsorption of such associates on the surface of Teflon significantly increases wetting before transition to spreading ($\theta = 8 - 10^{o}$).

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