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PHYSICAL CHEMISTRY OF SOLUTIONS

Hydrophobic Interactions between Polymethacrylic Acid and Sodium Laureth Sulfate in Aqueous Solutions

Z. M. Yaremko, L. B. Fedushinskaya, O. A. Burka, and M. N. Soltys
Ivan Franko National University, Lviv, 79000 Ukraine
e-mail: zyaremko@franko.lviv.ua

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Abstract—The role of hydrophobic interaction in the development of associative processes is demonstrated, based on the concentration dependences of the viscosity and pH of binary solutions of polymethacrylic acid as an anionic polyelectrolyte and sodium laureth sulfate as an anionic surfactant. It is found that the inflection point on the dependence of the difference between the pH values of binary solutions of polymethacrylic acid and sodium laureth sulfate on the polyelectrolyte concentration is a criterion for determining the predominant contribution from hydrophobic interaction, as is the inflection point on the dependence of pH of individual solutions of polymethacrylic acid on the polyelectrolyte concentration.

Keywords: polymethacrylic acid, sodium laureth sulfate, binary solutions, hydrophobic interaction, association.

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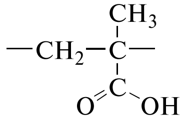
INTRODUCTION

The considerable interest in searching for effective new ways of controlling the targeted physicochemical properties of composite materials at the micro- and nanolevels is due to modern nanotechnologies. One of these proposes using mixtures of polyelectrolytes (PEs) and low-molecular surface active agents (SAAs), due to their adsorption from solutions on solid surfaces [1]. The properties of solid surfaces and the intermolecular interaction between components in the liquid phase both determine the course of adsorption. Studies of intermolecular interactions in binary aqueous solutions of PEs and SAAs remain a vital task in today's physical chemistry of solutions. These focus mainly on investigating interaction between PE macromolecules and oppositely charged SAA molecules [2–16], with solutions containing negatively charged PE macromolecules and positively charged SAA molecules being investigated more and more often [2–13] while the properties of binary solutions with positively charged PE macromolecules and negatively charged SAA molecules [14–16] remain less studied. It was shown in such works that the properties of binary solutions are determined by the interrelation of Coulomb and hydrophobic interactions. Studies of interactions in binary solutions of PEs and indentically charged SAAs have only just begun, with the results from investigating the interaction of components in binary solutions of anionic PEs and SAAs being presented in [17, 18].

The results from studying the intermolecular interactions between polymethacrylic acid (PMAA) as an anionic PE and sodium laureth sulfate (SLES) as an anionic SAA are discussed in this work.

EXPERIMENTAL

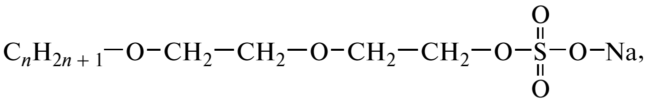
A PMAA macromolecule consists of units with a molecular weight of 86 g/mol:



$$-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{O^{\nearrow}C^{\searrow}OH}{|}}{C}}-$$

In aqueous solutions, PMAA has the properties of a weak electrolyte and is a good model object for studying both Coulomb interaction due to the dissociation of –COOH carboxylic groups and hydrophobic interaction, due to the presence of hydrophobic $-CH_3$ groups. The degree of polymerization of the studied PMAA sample was 350.

SLES has the following structural formula



$$C_nH_{2n+1}-O-CH_2-CH_2-O-CH_2-CH_2-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-Na,$$

where $n = 12–14$. SLES has the properties of a strong electrolyte in aqueous solutions. Its critical micelle concentration (CMC) is 3.84 mmol/L [19].

Bidistilled water with a specific conductivity of no higher than 0.25 mS/m was used to prepare individual and binary solutions of PMAA and SLES. To achieve equilibrium, the investigated solutions were preliminary held in a thermostat at 25°C for 3 h. The dependences of pH of binary and individual solutions of PMAA and SLES on their concentrations were stud-

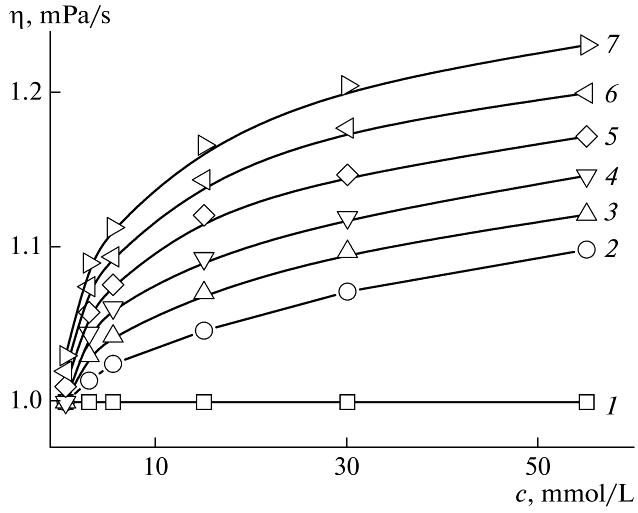


Fig. 1. Dependences of the relative viscosity of binary PMAA and SLES solutions on PMAA concentration at varying SLES content, mol/L: 0 (*1*), 0.05 (*2*), 0.5 (*3*), 1.0 (*4*), 2.0 (*5*), 4.0 (*6*), and 9.0 (*7*).

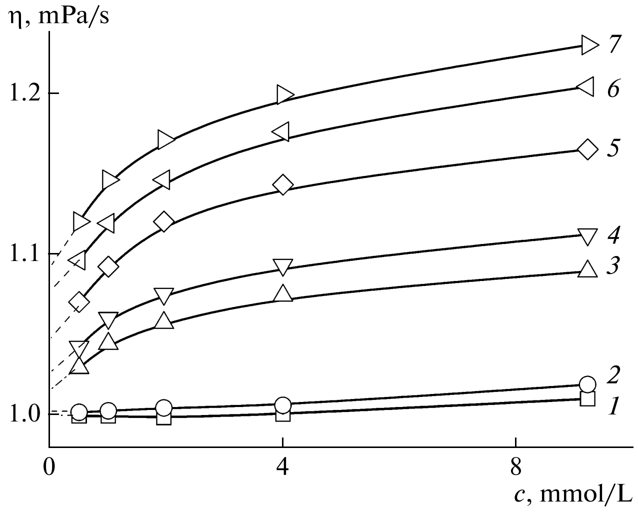


Fig. 2. Dependences of the relative viscosity of binary PMAA and SLES solutions on SLES concentration upon varying the PMAA content, mol/L: 0 (*1*), 0.55 (*2*), 3.0 (*3*), 5.5 (*4*), 15.0 (*5*), 30.0 (*6*), and 55.0 (*7*).

ied potentiometrically. The relative viscosities of the systems under study were determined using a capillary viscometer. Measurements of optical density of both individual and binary solutions of PMAA and SLES conducted at a wavelength of 540 nm showed that they were optically transparent over the investigated range of concentrations; i.e., these solutions contained no supramolecular formations that scatter light.

RESULTS AND DISCUSSION

For a long time, binary solutions of identically charged PEs and SAAs remained unstudied because it was assumed there was no interaction between their molecules. In such solutions, the Coulomb repulsion of identically charged groups does not favor association of their molecules; however, hydrophobic interaction can contribute to it under certain conditions. Conditions favorable to hydrophobic interaction between the hydrocarbon chains of SLES and the hydrophobic $-CH_3$ groups of PMAA arise in binary solutions of PMAA and SLES. At present, there is no quantitative description of hydrophobic interaction in aqueous solutions, but it is obvious that ionized molecules of SLES bound by hydrocarbon chains with hydrophobic $-CH_3$ groups of PMAA will raise the density of the negative charge in the volume of a PMAA molecule. Such increases in the density of negative charge of PMAA macromolecules are in turn responsible for two effects: an increase in the volume of macromolecules and a reduction in the degree of dissociation of –COOH carboxylic groups. Due to these processes, PMAA macromolecules in binary solutions attain a new state of equilibrium, changing their volume and the degree of ionization of –COOH carboxylic groups, relative to PMAA macromolecules in individual solutions. We have confirmed experimentally the occurrence of such effects in binary solutions of PMAA and SLES.

Changes in the volume of PMAA macromolecules in binary solutions due to hydrophobic interaction with SLES molecules can be evaluated from viscometry data. Our viscometry measurements conducted over the investigated range of concentrations did not reveal any change in the viscosity of individual solutions of PMAA (Fig. 1, curve *1*) and SLES (Fig. 2, curve *1*) upon an increase in their concentrations. At the same time, adding SLES to PMAA solutions substantially increases viscosity of binary systems (Figs. 1 and 2, curves *2*–*7* in both).

Einstein's fundamental equation of viscosity relates the relative viscosity of individual PMAA solutions, η_1/η_0, with the volume fraction of PE in solution, φ:

$$\eta_1/\eta_0 = 1 + \alpha\varphi, \qquad (1)$$

where α is a coefficient of proportionality.

The volume fraction of PMAA in solution is determined by the number of macromolecules, n, and their volume, V_1:

$$\varphi = nV_1. \qquad (2)$$

Inserting (2) into (1), we find the volume of macromolecules PMAA in an individual PE solution from the data on viscosity:

$$V_1 = \frac{\eta_1/\eta_0 - 1}{\alpha n}. \qquad (3)$$

Assuming that the change in the viscosity of binary solutions is due only to hydrophobic interaction between SLES molecules and PMAA macromole-

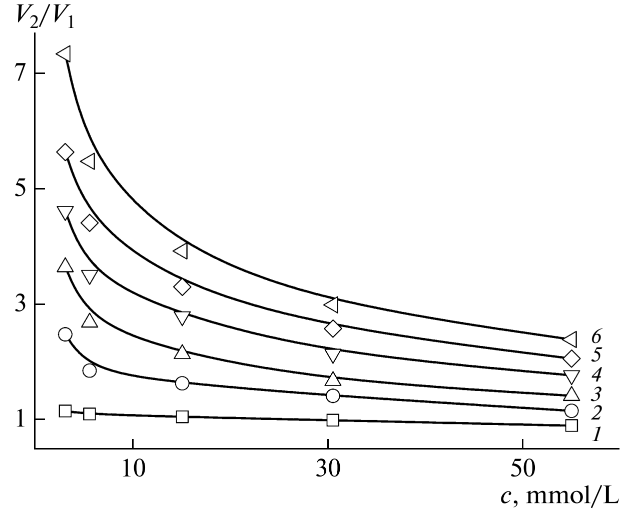


Fig. 3. Dependences of the relative increase in volume of PMAA macromolecules in binary PMAA and SLES solutions on PMAA concentration upon varying the SLES content, mol/L: 0.05 (*1*), 0.5 (*2*), 1.0 (*3*), 2.0 (*4*), 4.0 (*5*), and 9.0 (*6*).

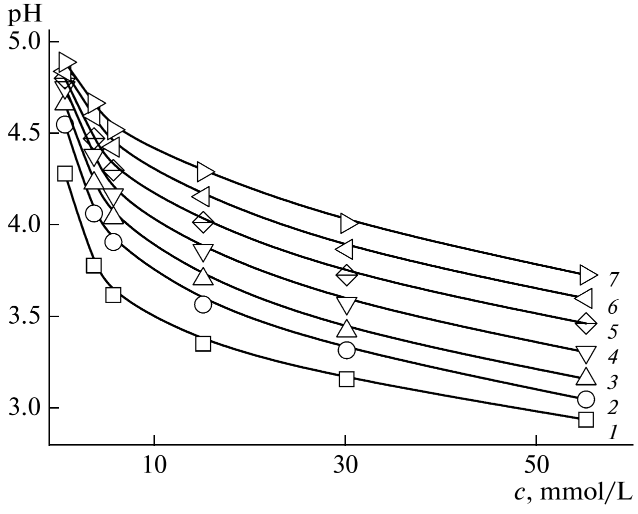


Fig. 4. Dependences of pH of binary PMAA and SLES solutions on concentration of carboxylic groups of PMAA upon varying the SLES content (denotation is the same as in Fig. 1).

cules, we can write an analogous equation for PMAA macromolecules in binary solutions, V_2:

$$V_2 = \frac{\eta_2/\eta_0 - 1}{\alpha n}, \tag{4}$$

where η_2/η_0 is the relative viscosity of the binary PMAA and SLES solutions.

Dividing (4) by (3), we find the relative increase in the volume of PMAA macromolecules in binary solutions that is due to their hydrophobic interaction with SLES molecules:

$$\frac{V_2}{V_1} = \frac{\eta_2/\eta_0 - 1}{\eta_1/\eta_0 - 1} = \frac{\eta_2 - \eta_0}{\eta_1 - \eta_0}. \tag{5}$$

To determine the relative increase in the volume of PMAA macromolecules in binary solutions, the viscosity of individual PMAA solutions, η_1, is estimated by extrapolating the dependence of the viscosity of binary solutions shown in Fig. 2 to zero SLES concentration.

Dependences of the relative increase in the volume of PMAA macromolecules in binary solutions are compared to their volumes in individual solutions in Fig. 3. As follows from our results, as the ratio of SLES concentration to PMAA concentration rises, the volume of PE macromolecules in binary solutions grows considerably, relative to the volume of macromolecules in individual PMAA solutions. According to the law of mass action, the higher the ratio of SLES concentration to PMAA concentration, the greater the number of SLES molecules that form hydrophobic bonds and thereby contribute to the relative increase in the volume of PE macromolecules.

The change in the degree of dissociation of –COOH carboxylic groups in binary solutions relative to individual PMAA solutions can be judged from the change in the ratio of the hydrogen ion activity in an individual PE solution, a_1, to the hydrogen ion activity in binary PMAA and SLES solutions, a_2:

$$S = a_1/a_2. \tag{6}$$

Logarithmic transformation of Eq. (6) produces

$$\begin{aligned}\log S &= \log a_1 - \log a_2 = -\mathrm{pH}_1 - (-\mathrm{pH}_2) \\ &= \mathrm{pH}_2 - \mathrm{pH}_1 = \Delta\mathrm{pH},\end{aligned} \tag{7}$$

where pH_2 and pH_1 are the pH values of the binary PMAA and SLES solutions and individual PMAA solutions, respectively.

CONCLUSIONS

ΔpH values were determined (Fig. 5) on the basis of our experimental dependences for the ΔpH of binary solutions and individual PMAA solutions on PE concentration (Fig. 4). Analysis of the dependence of the ΔpH value on the concentrations of PMAA and SLES allows us to determine the change in the degree of dissociation of carboxylic groups in a system. If the degree of dissociation of –COOH carboxylic groups in a binary PMAA and SLES solution did not change relative to individual solutions of PMAA, then ΔpH would be 0. In fact, the $\Delta\mathrm{pH} = f(C)$ dependence has a maximum whose value grows with upon adding SLES to a binary solution. No maximum is observed at the lowest SLES concentration of 0.05 mol/L, due to the negligible change in the concentration of hydrogen ions. The emergence of a maximum on any dependence implies the presence of at least two factors simultaneously influencing the sought value, with one of them raising it while the other lowers it. In our

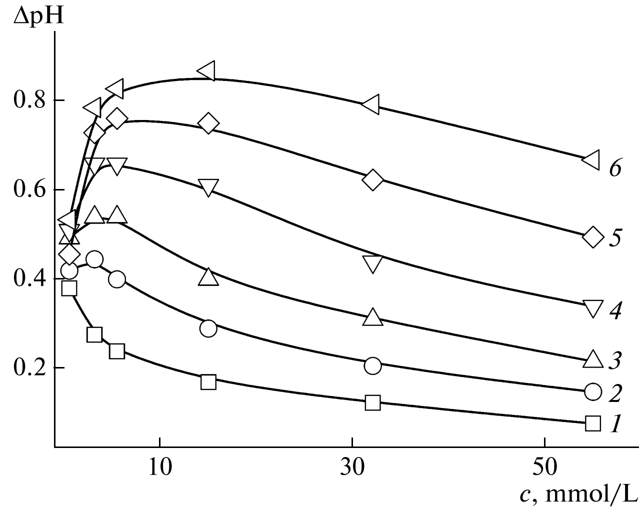


Fig. 5. Dependences of ΔpH of binary PMAA and SLES solutions on PMAA concentration upon varying the SLES content (denotation is the same as in Fig. 3).

binary solutions, the volume of macromolecules fell with a rise in the PMAA concentration at constant SLES concentrations (Fig. 3). The contraction of macromolecules, on the one hand, determines the drop in the degree of dissociation of –COOH carboxylic groups; on the other hand, due to a reduction in the number of bound SLES molecules, the density of the negative charge in the macromolecule volume diminishes and raises the degree of dissociation of –COOH carboxylic groups. These two factors result in the emergence of a minimum for the degree of dissociation of –COOH carboxylic groups, depending on the PMAA concentration. Because the concentration of hydrogen ions in the solution volume declines as the degree of dissociation of –COOH carboxylic groups falls, the ΔpH = *f*(*C*)pH of binary system rises; i.e., the minimum of the degree of dissociation of –COOH carboxylic groups corresponds to the maximum on the ΔpH = *f*(*C*) dependence.

Our viscometric and potentiometric studies of aqueous binary PMAA and SLES solutions therefore confirm the occurrence of hydrophobic interaction between SAA molecules with hydrophobic $-CH_3$ groups of PEs in binary solutions of identically charged SAAs and PEs.

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