Yessenov Science Journal
SCIENCE: RESEARCH AND PRACTICE

UDC 544.77
DOI 10.56525/EZAD5576

PROPERTIES OF WATER-SOLUBLE POLYMERS AND THEIR POLYCOMPLEXES IN AQUEOUS SOLUTIONS

BUSSURMANOVA A.
Caspian University of Technologies
and Engineering named after Sh.Yessenov
Aktau, Kazakhstan
E-mail: akkenzhe.bussurmanova@yu.edu.kz

Abstract. The interaction of oppositely charged polyelectrolytes (sodium salt of carboxymethylcellulose (NaCMC), methylcellulose (MC), polyethylenimine (PEI) and polydimethyldiallylammonium chloride (PDMDAAC), and unifloc (UF)) in an aqueous environment was studied using the methods of viscometry, spectrophotometry and macroelectrophoresis. It has been established that the interaction of these polyelectrolytes is accompanied by a significant decrease in reduced viscosity (up to 0.1-0.15 dl/g, which is typical for compacted macromolecules of globular proteins), an increase in optical density and an inversion of the sign of the electrokinetic potential. All this indicates the formation of interpolymer complexes from interacting cationic and anionic polyelectrolytes. Experimental results of studying the properties of water soluble polymers and their polyelectrolyte complexes in aqueous solutions at the water/air interface are described and discussed. It has been shown that complex formation in relatively simple systems is accompanied by changes in the pH of the medium, optical, hydrodynamic, electrochemical and other properties of macromolecules. In the systems we studied, the interaction of the system components is not accompanied by variations in the pH of the medium, therefore, information about the interaction of water-soluble polyelectrolytes in the systems we studied was obtained based on viscometric and spectrophotometric titration data, as well as from changes in the electrokinetic potential of macromolecules. The study of the electrokinetic potential showed that the formation of interpolymer complexes in the systems under consideration is accompanied by significant changes in the electrokinetic potential of macromolecules. A study of the properties of mixtures of aqueous solutions of Na-CMC, MC, UF with polydimethyldiallylammonium chloride and polyethylenimine indicates the formation of interpolyelectrolyte complexes that have a more compact structure than the original macromolecules.

Key words: polyelectrolytes; flocculation; cross-linking; stability; interpolymer complexes; optical density; polymer.

Introduction. The flocculating and structure-forming effects of water-soluble polyelectrolytes and their polycomplexes largely depend on the state of macromolecules in solution - in an expanded state (in dilute solutions), macromolecules, having significant hydrodynamic sizes, are prone to interact with a large number of particles of the dispersed phase

[1- 6]. This leads to aggregation of particles with each other, expressed in accelerated sedimentation of such aggregates (if the density of dispersed phase particles is higher than the density of the dispersion medium). Otherwise, this process is called flocculation.

Flocculation by polyelectrolytes depends on the state of ionization and concentration of macromolecules, the surface charge of dispersed phase particles.

At high concentrations, macromolecules coagulate and form compact globules [7, 8]. Such macromolecules, when adsorbed on the surface of particles of the dispersed phase, form dense layers that have structural and mechanical properties, and therefore stabilize the dispersed system.

Thus, a scientifically based approach to the selection of water-soluble polyelectrolytes and their polycomplexes for flocculation of particles from dilute suspensions and structuring in concentrated suspensions, in principle, should consist in a preliminary study of the properties of such polymers and their polycomplexes in dilute and concentrated aqueous solutions.

In this regard, in this work, the study of the effect of water-soluble polyelectrolytes and their interpolymer complexes on these suspensions was preceded by the study of these polymers in aqueous solutions.

The formation of interpolymer complexes in aqueous solutions of water-soluble polyelectrolytes has been quite well studied by foreign and Kazakh scientists. It has been shown that complex formation in relatively simple systems is accompanied by changes in the pH of the medium, optical, hydrodynamic, electrochemical and other properties of macromolecules. In the systems we studied, the interaction of the system components is not accompanied by variations in the pH of the medium; therefore, information about the interaction of water-soluble polyelectrolytes in the systems we studied was obtained based on viscometric and spectrophotometric titration data, as well as from changes in the electrokinetic potential of macromolecules.

Materials and research methods. The objects of research are the following water-soluble polymers: unifloc (UF) – a saponification product of polyacrylonitrile [9], sodium salt of carboxymethylcellulose (NaCMC) and methylcellulose (MC), polyethylenimine (PEI) and polydimethyldiallylammonium chloride (PDDMAAC).

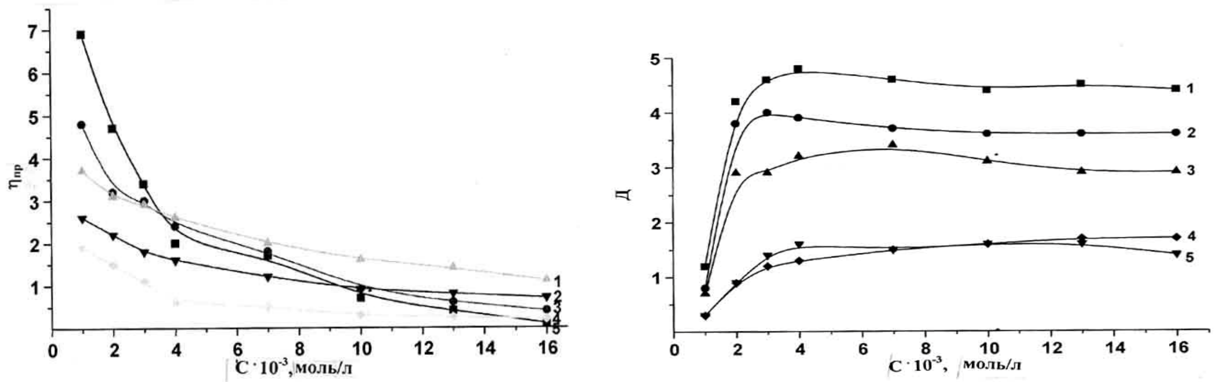
The choice of these polyelectrolytes as objects of study is due to the fact that, on the one hand, methylcellulose is a highly water-soluble polymer. On the other hand, unifloc and NaCMC are used due to the fact that they are obtained relatively simply from production waste and are widely available polymers. Polydimethyldiallylammonium chloride is a fairly well-studied polyelectrolyte and its practical applications are quite diverse, for example, it is a highly effective flocculating agent for water purification. The peculiarities of the interaction of UF with these polyelectrolytes are also important for the creation of modified forms of UF.

The work used aqueous solutions of polyelectrolytes with a concentration of 0.001-2.0 base mole/l. When calculating the concentration of the polymer in solution, the mass of the monomer unit of the macromolecule was taken as the molecular weight (i.e., the concentration was expressed as a basis - mole/l).

The stability of the interpolymer complex was judged by the change in the optical density of the system, which was determined on an SF-46 spectrophotometer. The electrophoretic mobility of particles was measured using the moving boundary method [10], and the value of the ξ-potential was calculated using the well-known Smoluchowski formula [10], i.e., without taking into account the polarization of the electric double layer, the contribution of which, under the conditions of our experiments, could be in the first approaching. The measurement error (ξ-potential) was 1 mV.

Results and Discussion. The formation of interpolymer complexes in aqueous solutions of water-soluble polyelectrolytes has been quite well studied by foreign and kazakhstani scientists. It has been shown that complex formation in relatively simple systems is accompanied by changes in the pH of the medium, optical, hydrodynamic, electrochemical and other properties of macromolecules. In the systems we studied, the interaction of the system components is not accompanied by variations in the pH of the medium, therefore, information about the interaction of water-soluble polyelectrolytes in the systems we studied was obtained based on viscometric and spectrophotometric titration data, as well as from changes in the electrokinetic potential of macromolecules.

In fig. 1 (a, b). The concentration dependences of the reduced viscosity ($\eta_{\text{red.}}$) and optical density (D) of aqueous solutions of water-soluble polymers - Uniflok, PDMDAAC, PEI, MC, Na-CMC - are presented.



a
1 - UF; 2 - PDMDAAC; 3 - PEI; 4 - Na-CMC; 5 - MC

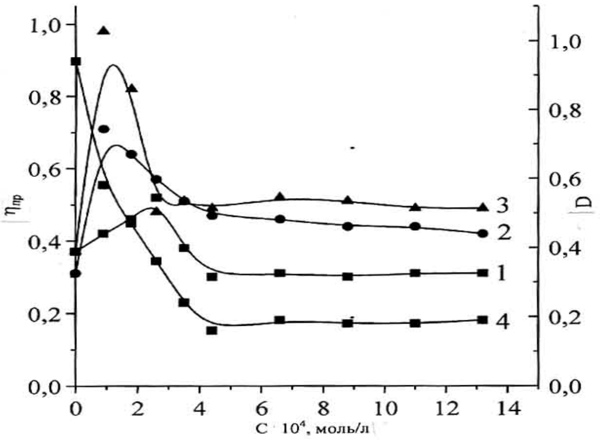
b
1 - UF; 2 - PDMDAAC; 3 - PEI; 4 - Na-CMC; 5 - MC

Figure 1– Concentration dependences of reduced viscosity (a) and optical density (b) of aqueous solutions of polyelectrolytes

These data indicate the typical polyelectrolyte nature of these polymers: with dilution of the solution, the values of the reduced viscosity increase [11]. This is the phenomenon of polyelectrolyte swelling. It should be noted that the unfolding of macromolecules is accompanied by a decrease in the optical density of their aqueous solutions (Fig. 1 b).

In order to study the peculiarities of the formation of interpolymer complexes in mixtures of oppositely charged polyelectrolytes, in this work, the main attention was paid to studying the change in A and D of aqueous solutions of anionic polyelectrolytes - Na-CMC, MC and UV, when titrated with cationic polyelectrolytes PEI (weakly basic) and PDMDAAC (strongly basic).

Figure 2 shows the curves of viscometric and turbidimetric titration of Na-CMC and MC with the indicated polycations.



1 - Na-CMC; 2 - Na-CMC/ PEI; 3 - Na-CMC/ PDMDAAC; 4 - Na-CMC/PDMDAAC

Figure 2 – Dependence of optical density (1-3) and reduced viscosity (4) of aqueous solutions of Na-CMC during titration with PDMDAAC and PEI

It can be seen from the figure that with an increase in the relative concentration (n) of interacting polyelectrolytes $\eta_{\text{red.}}$ decreases significantly, reaching extremely small (0.1 dl/g) values. Such low values of reduced viscosity are usually characteristic of compact (globular) macromolecules. The reaction of the formation of a complex of sodium salt of carboxymethylcellulose with PDMDAAC can be represented as follows:

$$C_8H_{16}N^+Cl + C_6H_7O_2(OH)_{3-x}(OCH_2COONa)_x \longrightarrow C_8H_{16}N_+(COO^-CH_2O)_x(OH)_{3-x}O_2H_7C_6 + NaCl$$

It follows from the reaction equation that the driving force for the formation of interpolymer complexes in the systems under consideration is the electrostatic interactions of oppositely charged functional groups of macromolecules stabilized by hydrophobic interactions and hydrogen bonds (H-bonds).

To obtain further information about the complexation mechanism of water-soluble polyelectrolytes, the electrokinetic potential was studied. Studies have shown that the formation of interpolymer complexes in the systems under consideration is accompanied by significant changes in the electrokinetic potential of macromolecules (Fig. 3).

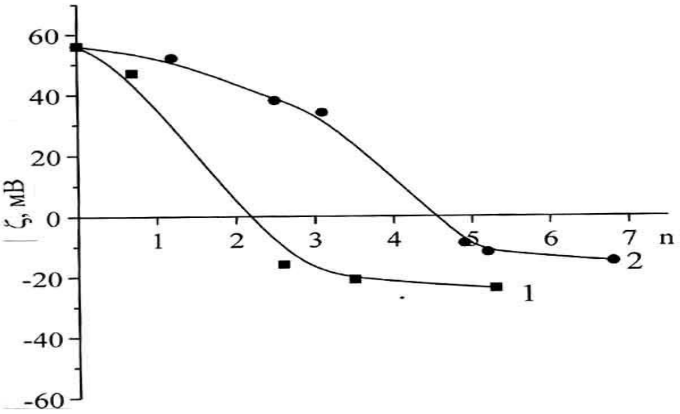


Figure 3 – Electrokinetic potential of aqueous solutions of Na-CMC with PDMDAAC (1) and PEI (2)

As can be seen from the figure, titration of an aqueous solution of polycations with Na-CMC leads to a decrease in the positive ζ - potential, and then, at large values of n, to recharging of the resulting particles of the interpolymer complex [12]. Moreover, the higher the charge density of the polycation (PDMDAAC), the earlier (on the n scale) this process occurs. This indicates a greater efficiency of the interaction of Na-CMC with PDMDAAC compared to PEI.

The interaction of UF with PDMDAAC occurs somewhat differently (Fig. 4). In this case, the formation of the interpolymer complex, although accompanied by a significant decrease in reduced viscosity (up to 0.1), however, the optical density initially increases slightly, and then, in the range of 0.25 n 1.0, decreases significantly, reaching plateau in the region of n 1.5. Such complex dependences D (n) = f (n) are apparently associated with the blocking of charged groups of PDMDAAC by unifloc and their neutralization in the n region of 0.2-0.3. After this, the introduced excess polyampholyte ions recharge the surface of the complex, lyophilizing it [13, 14].

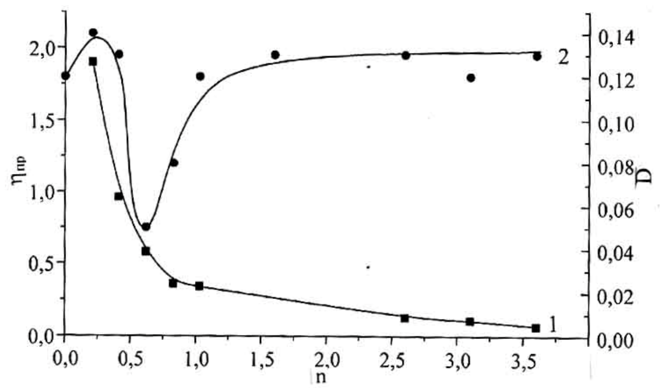


Figure 4 – Change of reduced viscosity (1); optical density (2) during titration of unifloc with PDMDAAC

It can be assumed that the functional groups of the polycation interact with the COON groups of the unifloc as the most strongly dissociated groups by change. This can lead to an imbalance in the ratio of positively and negatively charged groups of unifloc macromolecules. The predominant contribution of electrostatic interactions in the formation of the interpolymer complex of unifloc with the polycations under consideration is evidenced by changes in the ζ -potential of macromolecules (Fig. 5).

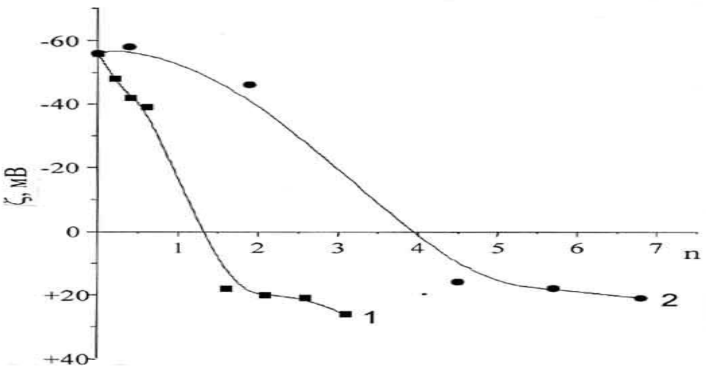


Figure 5 – Dependence of the electrokinetic potential of UF macromolecules on the relative concentration of PDMDAAC (1) and PEI (2)

Titration of an aqueous solution of unifloc with polycations is accompanied first by a significant decrease in the potential of UF macromolecules, and then by their recharging. In this case, the highly charged polycation (PDMDAAC), as in the previous case, at significantly lower n values than PEI, leads to recharging of the interpolymer complex.

Thus, the study of the properties of mixtures of aqueous solutions of Na-CMC, MC, UF with polydimethyldiallylammonium chloride and polyethylenimine indicates the formation of interpolyelectrolyte complexes that have a more compact structure than the original macromolecules.

Conclusion. Due to the phenomenon of polyelectrolyte swelling, the reduced viscosity values increase in dilute solutions of polyelectrolytes. In this case, the unfolding of macromolecules is accompanied by a decrease in the optical density of their aqueous solutions.

With increasing relative concentration (n) of interacting polyelectrolytes, the reduced viscosity decreases significantly, reaching extremely low values. Such low values of reduced viscosity are usually characteristic of compact (globular) macromolecules.

Titration of an aqueous solution of polycations with Na-CMC leads to a decrease in the positive ζ - potential, and then, at large values of n, to a recharge of the resulting particles of the interpolymer complex.

When UF interacts with PDMDAAC, an interpolymer complex is formed, and the reduced viscosity decreases, but the optical density first increases slightly, and then, in the range of $0{,}25 \leq n \leq 1{,}0$, decreases significantly, reaching a plateau in the region of $n \geq 1{,}5$. Such complex dependences D (n) = f (n) are apparently associated with the blocking of charged groups of PDMDAAC by unifloc and their neutralization in the n region of 0.2-0.3.

Thus, the study of the properties of mixtures of aqueous solutions of Na-CMC, MC, UF with polydimethyldiallylammonium chloride and polyethylenimine indicates the formation of interpolyelectrolyte complexes that have a more compact structure than the original macromolecules.

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Бусурманова Аккенже
Ш.Есенов атындағы Каспий технологиялар және инжиниринг университеті
Ақтау қ., Қазақстан

СУДА ЕРИТІН ПОЛИМЕРЛЕР МЕН ОЛАРДЫҢ ПОЛИКОМПЛЕКСТЕРІНІҢ СУЛЫ ЕРІТІНДІДЕГІ ҚАСИЕТТЕРІ

Аңдатпа. Қарама-қарсы зарядталған полиэлектролиттердің (карбоксиметилцеллюлозаның натрий тұзы (Na-КМЦ), метилцеллюлоза (МЦ), полиэтиленимин (ПЭИ) және полидиметилдиалиламмоний хлориді (ПДМДААХ), унифлок (УФ)) сулы ортадағы өзара әрекеттесуі вискозиметрия, спектрофотометрия және макроэлекторфорез әдістерінің көмегімен зерттелді. Бұл полиэлектролиттердің өзара әрекеттесуі келтірілген тұтқырлықтың айтарлықтай төмендеуімен (0,1-0,15 дл/г дейін, глобулярлы белоктардың тығыздалған макромолекулаларына тән), оптикалық тығыздықтың жоғарылауымен және электрокинетикалық потенциал белгісінің инверсиясымен жүретіні анықталды. Осының барлығы өзара әрекеттесетін катиондық және анионды полиэлектролиттерден интерполимерлі комплекстердің түзілуін көрсетеді. Суда еритін полиэлектролиттердің және олардың су/ауа бөлу шекарасындағы сулы ерітінділердегі полиэлектролиттік комплекстерінің қасиеттерін зерттеудің тәжірибелік нәтижелері сипатталған және талқыланған. Салыстырмалы түрде қарапайым жүйелерде комплекс түзілу ортаның pH, макромолекулалардың оптикалық, гидродинамикалық, электрохимиялық және басқа қасиеттерінің өзгеруімен қатар жүретіні көрсетілген. Зерттелетін жүйелерде жүйе компоненттерінің өзара әрекеттесуі ортаның pH өзгеруімен қатар жүрмейді, сондықтан осы зерттеген жүйелердегі суда еритін полиэлектролиттердің өзара әрекеттесуі туралы ақпарат вискозиметриялық және спектрофотометриялық титрлеу негізінде, сондай-ақ, макромолекулалардың электрокинетикалық потенциалының өзгеруінен деректер алынды. Электркинетикалық потенциалды зерттеу қарастырылып отырған жүйелерде интерполимерлі комплекстердің түзілуі макромолекулалардың электрокинетикалық потенциалының елеулі өзгерістерімен жүретінін көрсетті. Na-КМЦ, МЦ, УФ сулы ерітінділерінің полидиметилдиалиламмоний хлориді және полиэтилениминмен қоспаларының қасиеттерін зерттеу бастапқы макромолекулаларға қарағанда ықшам құрылымға ие интерполиэлектролиттік кешендердің түзілуін көрсетеді.

Кілт сөздер: полиэлектролиттер; флокуляция; құрылым түзілу; тұрақтылық; интерполимерлік комплекстер; оптикалық тығыздық; полимер.

Бусурманова Аккенже
Каспийский университет технологий и инжиниринга им. Ш.Есенова
г.Актау, Казахстан

СВОЙСТВА ВОДОРАСТВОРИМЫХ ПОЛИМЕРОВ И ИХ ПОЛИКОМПЛЕКСОВ В ВОДНЫХ РАСТВОРАХ

Аннотация. Изучено взаимодействие противоположно заряженных полиэлектролитов (натриевой соли карбоксиметилцеллюлозы (Na-КМЦ), метилцеллюлозы (МЦ), полиэтиленимина (ПЭИ) и хлорида полидиметилдиаллиламмония (ПДМДААХ), унифлока (УФ)) в водной среде методами вискозиметрии, спектрофотометрии и макроэлектрофореза. Установлено, что взаимодействие этих полиэлектролитов сопровождается значительным снижением приведенной вязкости (до 0,1-0,15 дл/г, что характерно для компактированных макромолекул глобулярных белков), увеличением оптической плотности и инверсией знак электрокинетического потенциала. Все это указывает на образование интерполимерных комплексов из взаимодействующих катионных и анионных полиэлектролитов. Описаны и обсуждены экспериментальные результаты исследования свойств водорастворимых полиэлектролитов и их полиэлектролитных комплексов в водных растворах на границе раздела вода/воздух. Показано, что комплексообразование в относительно простых системах сопровождается изменением pH среды, оптических, гидродинамических, электрохимических и других свойств макромолекул. В исследованных системах взаимодействие компонентов системы не сопровождается изменением pH среды, поэтому информация о взаимодействии водорастворимых полиэлектролитов в изученных нами системах получена на основе данных вискозиметрического и спектрофотометрического титрования, а также от изменения электрокинетического потенциала макромолекул. Исследование электрокинетического потенциала показало, что образование интерполимерных комплексов в рассматриваемых системах сопровождается существенными изменениями электрокинетического потенциала макромолекул. Исследование свойств смесей водных растворов Na-КМЦ, МЦ, УФ с хлоридом полидиметилдиаллиламмония и полиэтиленимином указывает на образование интерполиэлектролитных комплексов, имеющих более компактную структуру, чем исходные макромолекулы.

Ключевые слова: полиэлектролиты; флокуляция; структурообразование; стабильность; интерполимерные комплексы; оптическая плотность; полимер.