

Aggregates of sodium hyaluronate with cationic and aminoxide surfactants in aqueous solution — light scattering study

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Abstract

Aggregation properties of sodium hyaluronate (NaHA) with different types of surfactants in aqueous sodium chloride solution have been studied by using static and dynamic light scattering method. Molecular weight, second virial coefficient, radius of gyration, and hydrodynamic radius have been calculated. The polymer — surfactant aggregate growth was found in complexes of NaHA with an ionic surfactant (dodecyltrimethylammonium bromide) and ionic, dimeric surfactants (dodecanediyl- α,ω -bis(dimethyloctylammonium bromide) and *N,N'*-bis(dodecyldimethyl)-4,13-dioxo-3,14-dioxahexadecane-1,16-diyldiammonium dibromide). In case of dodecyldimethylamine oxide (DDAO), the decreasing molecular weight and aggregate size of the NaHA — DDAO complex with increasing DDAO concentration were found above the surfactant critical micelle concentration, indicating the absence of electrostatic interactions between NaHA and DDAO that would lead to the increase in aggregate size. This behaviour may be ascribed to the non-ionic character of DDAO. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Sodium hyaluronate; Dodecyltrimethylammonium bromide; Dimeric surfactant; Dodecyldimethylamine oxide; Polymer-surfactant complex; Light scattering; Molecular weight; Radius of gyration; Hydrodynamic radius

1. Introduction

Solution properties of sodium hyaluronate (NaHA) have been broadly discussed [1–4]. In

our last study [5], it was found that this anionic polysaccharide forms complex with cationic alkane-diyl- α,ω -bis(dimethylalkylammonium bromide) surfactant (referred to as dimeric surfactant), and molecular weight of the complex increases with surfactant concentration. Now, we extend our study to different types of surfactants interacting with NaHA.

Dodecyldimethylamine oxide (DDAO) forms

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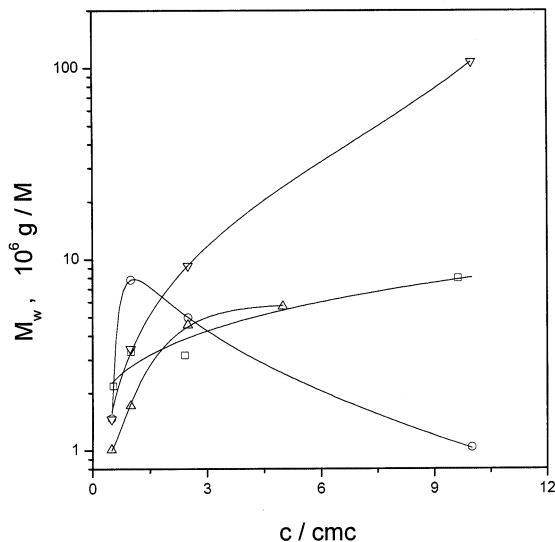


Fig. 1. Molecular weight M_w of NaHA-surfactant mixture in 0.25 M NaCl versus ratio c/cmc (c is the surfactant concentration). The surfactants used: \square 12-8-12, \circ DDAO, \triangle DTAB, and ∇ DC surfactant.

only spherical micelles in aqueous solution above its critical micelle concentration (cmc) [6]. Physi-

cal properties of DDAO micelles strongly depend on degree of protonation α and, hence, on pH [7,8]. It was found that dramatic changes in physical quantities of micelles like cmc [6], micelle molecular weight [9], liquid-liquid phase separation temperature [10], electrophoretic mobility [11], surface excess at the air-water interface [8,12], and counterion binding [13] occur in the half-protonated state, at $\alpha \sim 0.4$. The general explanation of such behaviour is given by the change of the electrostatic potential in the Stern layer of a micelle with α , suggesting continuous variation of non-ionic micelles to cationic ones and successive adsorption of electrolyte ions on micelles [10]. At higher α , adsorption of electrolyte ions on micelles is restrained. It was also observed that the dramatic changes of cmc dependent on degree of protonation occur in the presence of electrolyte (NaCl) in the solution

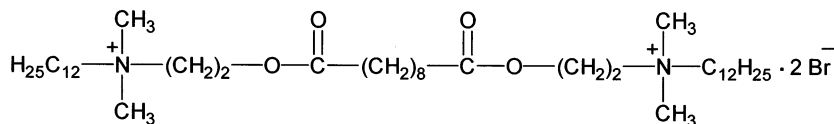
[9,12] but the hydrodynamic radius of DDAO micelles does not depend on electrolyte concentration [14].

Polymer-surfactant interactions are a subject of intensive research. Neutral, uncharged polymer — surfactant interactions [15–18] as well as charged polymer — conventional ionic surfactant interactions [19–24] have been studied. Interaction between positively charged polymer and anionic surfactant was found to be of electrostatic character [19–21]. It has also been found that ionic polymer — ionic surfactant systems are sensitive to precipitation depending on concentration of added electrolyte [19,20,22].

Interactions between NaHA and DDAO are of another type because of the non-ionic character of DDAO. Related systems of DDAO and hexadecyldimethylamine oxide with cinnamic acid were studied by neutron scattering [25,26]. Based on the interaction between weak base and weak acid, variety of aggregate structures (micelles, vesicles, and multilamellar layers) depending on the ratio of cinnamic acid/surfactant were found. Interactions were also studied between sodium polyacrylate and tetradecyldimethylamine oxide [27] and polyacrylic acid and tetradecyldimethylamine oxide [28]. It was found that physical properties of aggregates composed from polymer and surfactant depend on the degree of protonation of tetradecyldimethylamine oxide, which can be controlled by varying pH.

2. Materials and methods

Microbial NaHA was obtained from Contipro (Ústí n. Orlicí, Czech Republic). Dimeric surfactant $C_{12}H_{25}-(C_2H_6)N^+-C_8H_{16}-N^+(C_2H_6)-C_{12}H_{25} \cdot 2Br^-$ (referred to as 12-8-12) was prepared by the reaction of tertiary diamine with 1-bromoalkane as described previously [29]. The product was purified by manifold crystallization from acetone-methanol mixture. Thin layer chromatography and elementary analysis confirmed sample identity. The dimeric surfactant, N,N' -bis(dodecyldimethyl)-4,13-dioxo-3,14-dioxahexadecane-1,16-diylidiammonium dibromide, referred to as DC surfactant (see the following structure)



was synthesized from the corresponding α,ω -alkanedicarboxylic acid. The procedure and spectral characteristics of the compound have been published elsewhere [30]. DDAO was prepared by the reaction of the appropriate tertiary amine dissolved in isopropyl alcohol with aqueous solution of hydrogen peroxide and was recrystallized from dry acetone [31]. Commercial sample of dodecyltrimethylammonium bromide (DTAB) was recrystallized twice from acetone-methanol mixture.

Otsuka Electronics dynamic light scattering photometer DLS-700 with the argon laser (optical laser power 15 mW, wavelength 488 nm) was used for light scattering measurements. The cell housing was filled with di-*n*-butylphthalate and kept at 25°C. Solvent and solutions were filtered three times through Millipore membrane filters.

Static light scattering from a polymer solution is described by the relation

$$\frac{Kc}{R(q)} = \frac{1}{M_w P(q)} + 2A_2 c \quad (1)$$

where $R(q)$ is the reduced intensity, c is a polymer concentration, A_2 is the second virial coefficient, $P(q)$ is the particle scattering factor, and M_w is the weight average molecular weight. The optical constant K is given as follows;

$$K = \frac{4\pi^2 n_0^2 (dn/dc)^2}{N_a \lambda^4} \quad (2)$$

where n_0 is the refractive index, dn/dc is the refractive index increment, N_a is the Avogadro constant, and λ is the wavelength of the incident beam. The inverse value of the particle scattering factor $1/P(q)$ can be expanded into series in the following way;

$$\frac{1}{P(q)} = 1 + \frac{1}{3} q^2 R_G^2 + \dots \quad (3)$$

R_G is the radius of gyration. The angle dependent quantity q is of the following meaning;

$$q = \frac{4\pi n_0}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (4)$$

θ is the scattering angle. The double extrapolation of the right side of Eq. (1) to zero angle and zero concentration gives the value of $1/M_w$ on the Kc/R axis.

Hydrodynamic diameter d is obtained from the dynamic light scattering measurements. For a monodisperse solution of non interacting particles, the first-order electric field time correlation function $g_1(t)$ at time t relates to the translational diffusion coefficient D as follows;

$$g_1(t) = A \exp(-2\Gamma t) \\ \Gamma = Dq^2 \quad (5)$$

where Γ is the decay constant and A is a constant. Finally

$$d = \frac{kT}{3\pi\eta_0 D} \quad (6)$$

where T is the temperature, k is the Boltzmann constant, and η_0 is the solvent viscosity.

3. Results and discussion

In the previous paper [5], we dealt with aggregates consisting of NaHA, dimeric quaternary ammonium surfactant 12-8-12 (12 carbon atoms in each of the alkyl chains and eight carbon atoms in the spacer) and NaCl. According to the static light scattering results, we have found that molecular weight of such aggregate increases at high surfactant concentration and the second virial coefficient decreases. It indicates the growth of the polymer-surfactant complex and the electrostatic neutralization of NaHA by the complex formation with cationic surfactant.

In Fig. 1, the molecular weights of aggregates consisting of NaHA and different kinds of surfactants are shown as a function of surfactant con-

centration relative to cmc (c/cmc) and compared with those of NaHA — 12-8-12 complex. Surfactants are a single-chain cationic ammonium surfactant (DTAB), a double-chain surfactant based on two carboxylic groups (DC surfactant), and DDAO. The increase in molecular weight of NaHA complex with single- and double-chain ammonium surfactants becomes moderate at high surfactant concentration. It indicates that the number of surfactant monomers in the complex is saturated. The saturation occurs at low concentration in a case of DTAB, but the continuous increase in molecular weight is observed even at c/cmc ten for NaHA — DC surfactant complex. It is assumed that the long spacer of DC surfactant (16 atoms; see the formula in the experimental section) bends into the hyaluronate coil core because of the hydrophilicity of the spacer due to the two carboxylic groups. This fact has been confirmed by the solubility experiments: It was found that the solubility of DC surfactant is much higher than that of the conventional ammonium surfactants.

The complex of NaHA with DDAO reaches its maximum molecular weight exactly at surfactant cmc. Its behaviour with increasing surfactant concentration is different in comparison with other investigated surfactants. The molecular weight of the complex is decreased with increasing surfactant concentration above the cmc. The interaction between NaHA and non-ionic DDAO micelle must be hydrogen-bonding but not electrostatic. Above the cmc, this interaction is restrained owing to the favourable formation of free DDAO micelle in the aqueous medium and successive decrease of average molecular weight in the mixture of NaHA and DDAO is observed.

It was documented by strong viscosity increase that tetradecyldimethylamine oxide protonated at low pH interacts in the form of rodlike micelles with charged polymer (polyacrylic acid) [28]. However, there is difference between the cited case and the presented study. DDAO used here forms only spherical micelle [6] and is not protonated in the present condition. Therefore, non-ionic DDAO micelles do not form large complexes with NaHA that would result in remarkable increase of viscosity.

The second virial coefficient A_2 calculated on the

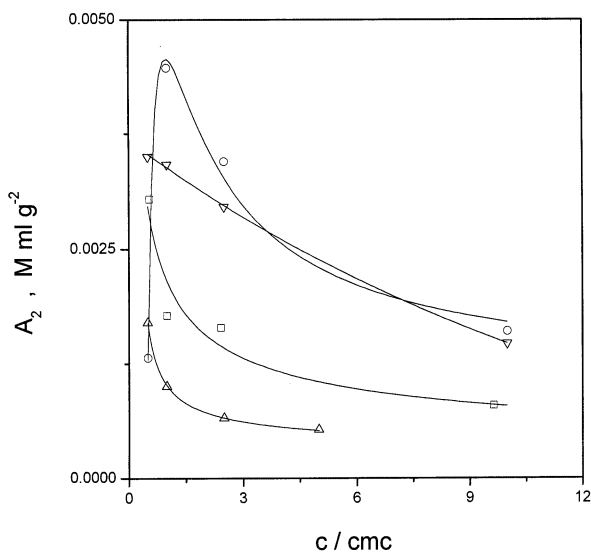


Fig. 2. Second virial coefficient A_2 of NaHA-surfactant mixture in 0.25 M NaCl versus ratio c/cmc . The surfactants used: \square 12-8-12, \circ DDAO, \triangle DTAB, and ∇ DC surfactant.

basis of Eq. (1) is shown in Fig. 2 as a function of c/cmc . The second virial coefficient decreases with increasing c/cmc for three investigated complexes, except for the DDAO aggregate. Based on the investigations of single-chain ammonium surfactants [32–36], the decrease of the second virial coefficient indicates the decrease of electrostatic repulsive interaction. Since the decrease goes side by side with the increase in molecular weight of polymer-surfactant complex, it originates in the electrostatic binding of cationic surfactant on anionic NaHA. For the NaHA-DDAO mixture, there was a maximum of the second virial coefficient at cmc as well as the case of molecular weight depicted in Fig. 1. Although the results of complex with DDAO indicate the polymer-micelle interaction at $c \sim cmc$, the essence of the virial coefficient is not clear.

In Fig. 3, the radius of gyration R_G on c/cmc is depicted. The dependencies of R_G on c/cmc for NaHA complexes with dimeric surfactant 12-8-12 and DTAB are constant at high surfactant concentrations. It corresponds with the saturation of molecular weight (Fig. 1) at the high ratio of c/cmc . It may be concluded that monomeric (DTAB) and dimeric (12-8-12) ammonium surfactants display

similar tendency in the formation of complex with anionic hyaluronate. Figs. 1–3 indicate the growth of the NaHA-ammonium surfactant complex with increasing surfactant concentration for both single- and double-chain surfactants resulting from the strong electrostatic interactions between oppositely charged polymer and surfactant. In the case of DC surfactant, it is probable that very large values of R_G as well as molecular weight at high surfactant concentrations indicate the presence of large aggregates. This assumption can be made based on the analogy with double-chained cationic ammonium surfactants with spacer lengths of 16 and 20 carbon atoms (12-16-12 and 12-20-12) that were found to form vesicles and membrane sheets [37]. In our case, the spacer length of 16 atoms is long enough to be bent into the hydrophobic core, to decrease the value of area per surfactant dimer, and to induce the aggregate growth. It also may be noted that the formation of large aggregates at high surfactant concentrations is the property of surfactant structure resulting from the long spacer length and primarily may not be ascribed to the polymer-surfactant interactions. The interaction between DC surfactant and NaHA should be of the same type as of systems with DTAB and 12-8-12 surfac-

tants. We found the decreasing value of R_G of NaHA complex with DDAO (Fig. 3), above the surfactant cmc, as well as the decreasing molecular weight of DDAO-NaHA aggregate. This indicates the coexistence of free DDAO micelles.

It is possible to calculate the surfactant-to-polymer charge ratio for ionic surfactant or the binding ratio per polymer charge for DDAO ρ in NaHA system with surfactant under the assumption that surfactant micelles may be incorporated into NaHA coils. The final equation described in the previous publication [5] is given as follows;

$$\rho = An_{ps}/n_p \quad (7)$$

where $n_{ps} = (M_{ps} - M_p)/M_{s0}$ is the number of surfactant unit in NaHA aggregate and $n_p = M_p/M_{p0}$ is the number of disaccharidic unit in NaHA. M_{ps} ($= M_w$), M_p , M_{s0} , and M_{p0} are the molecular weights of NaHA-surfactant complex, NaHA without surfactant addition, surfactant, and one disaccharidic unit, respectively. Factor $A = 1$ for DTAB and DDAO, and $A = 2$ for double chained surfactants of 12-8-12 and DC surfactant. Then, the number of micelles bound on NaHA is calculated as n_{ps}/n , where n is a micelle aggregation number. The calculated numerical values are listed in Table 1, where analytical data from light scattering are included.

The adsorption of 12-8-12 and DC surfactant on NaHA around $c/cmc = 1$ is close to electroneutrality, whereas negative charge dominates in DTAB-NaHA complex at $c/cmc = 1$. It is obvious that with increasing concentration, three surfactants adsorb on NaHA more abundant than neutral, indicating the formation of micelles on NaHA. The situation of excess adsorption is same even at the NaHA complex with DDAO. The number of micelles adsorbed on NaHA was calculated under the assumption that all surfactants adsorb on NaHA as micelles and the micelle size on NaHA is same as that of free micelle prepared in aqueous medium. As seen in Table 1, the number of micelles on NaHA is larger for the complex with 12-8-12 than for the complex with DTAB. Nevertheless, the NaHA-12-8-12 complex must shrink, as estimated from the small hydrodynamic.

The dynamic scattering data reported in Table 1

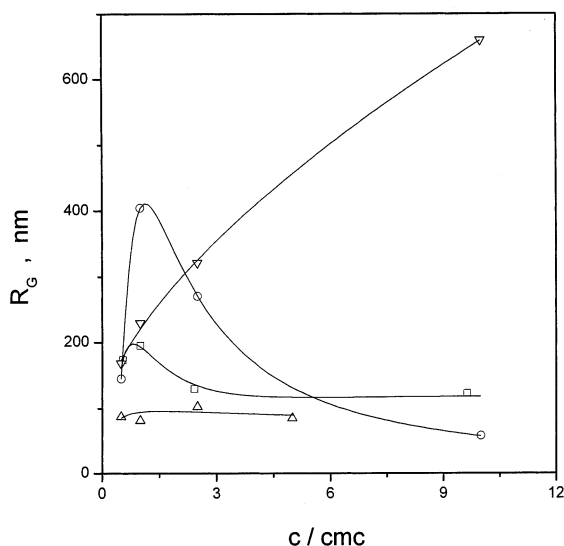


Fig. 3. Radius of gyration R_G of NaHA-surfactant mixture in 0.25 M NaCl versus ratio c/cmc . The surfactants used: □ 12-8-12, ○ DDAO, △ DTAB, and ▽ DC surfactant.

Table 1

Polymer-surfactant aggregate parameters obtained by static light scattering method in system 0.1 %wt NaHA, 0.25 M NaCl and different types of surfactants^a

c/cmc	M_w (10^6 gM ⁻¹)	A_2 (10^{-3} M ml g ⁻²)	R_G (nm)	d_{90} (nm)	n_{ps}	ρ	n_{ps}/n
<i>(a) DTAB (cmc = 14 mM, n = 60.5)^b</i>							
0.5	1.01	1.7	87	52			
1.0	1.71	1.0	81	48	641	0.2	11
2.5	4.56	0.7	102	62	9880	2.6	163
5.0	5.69	0.5	85	46	13 600	3.5	224
<i>(b) 12-8-12^c (cmc = 0.83 mM, n = 23)^d</i>							
0.54	2.18	3.0	174	17	959	0.5	
1.00	3.30	1.8	195	57	2560	1.3	111
2.41	3.17	1.6	130	51	2380	1.2	103
9.64	7.96	0.8	123	18	9230	4.8	401
<i>(c) DC surfactant (cmc = 0.29 mM)^e</i>							
0.5	1.45	3.5	168	72			
1.0	3.42	3.4	230	60	2270	1.1	
2.5	9.24	3.0	321	58	9170	4.7	
10.0	107.00	1.0	659	58	12 6000	64.1	
<i>(d) DDAO (cmc = 1.9 mM, n = 96)^f</i>							
0.5	1.47	1.3	145	110			
1.0	7.82	4.5	404	114	27 500	7.0	286
2.5	4.98	3.5	271	104	15 100	3.9	158
10.0	1.03	1.6	58	28			

^a c/cmc, surfactant concentration relative to cmc; M_w , molecular weight; A_2 , second virial coefficient; R_G , radius of gyration; d_{90} , hydrodynamic diameter; n_{ps} , number of surfactant monomers bound on NaHA; ρ , surfactant-to-polymer charge ratio; n_{ps}/n , number of micelles bound on NaHA; and n , micelle aggregation number.

^b Ref. [31].

^c Ref. [5].

^d Ref. [36].

^e Ref. [30].

^f Ref. [9].

and presented in Fig. 4 have been obtained with Eq. (5), which is strictly valid for monodisperse solutions. On the other hand, if the solution is quite polydisperse, measurements performed at the scattering angle of 90° may strongly underestimate the average hydrodynamic radius. Then, the dynamic measurements can be used mainly to gain qualitative information about the system. When compared with R_G , which is a true average since it is obtained with an extrapolation to zero angle, the fact that all R_G data are larger than d_{90} means that the solution is quite polydisperse with small aggregates coexisting with large aggregates, the dimension of which is comparable with the wavelength of the laser light. Small and large aggregates, respectively, correspond to NaHA

species with small and large numbers of adsorbed surfactant.

The inconsistency of R_G and d_{90} (hydrodynamic diameter at 90°) data is especially strict in the case of the DC surfactant. Fig. 3 shows that R_G grows steeply with concentration, while d_{90} in Fig. 4 remains practically constant. This is a strong indication of an increase of the relative amount of large aggregates in the system. It is trivial to explain the decrease of d_{90} of the complex with double-chain cationic surfactant 12-8-12. The micelles shrink at high concentration, as discussed before [5]. On the other hand, the decrease of d_{90} of the complex with DDAO originates in the formation of free DDAO micelles, which is the same reason for the decrease of molecular weight and radius of gyration.

4. Conclusions

The molecular weights of NaHA complex with single- (DTAB) and double-chain (12-8-12) ammonium surfactants moderately increase with surfactant concentration, indicating the adsorption of surfactant on NaHA. The variation of positive charge of dimeric surfactant unit per one negative charged hyaluronate disaccharidic unit in the NaHA-surfactant complex indicates that the increased adsorption of surfactant with increasing surfactant concentration is observed.

In case of the NaHA complex with DC surfactant, the steep increase in molecular weight and radius of gyration and the decrease of the second virial coefficient at high surfactant concentration were observed. This may be ascribed to the tendency of surfactant to form large aggregates in this concentration region.

The molecular weight of the NAHA-DDAO complex reaches its maximum at $c/cmc = 1$ and decreases with increasing surfactant concentration above cmc. Other quantities related to the aggregate size (radius of gyration and hydrodynamic diameter) also decrease with increasing DDAO concentration above the $c/cmc = 1$ region. This

indicates the formation of NaHA-DDAO aggregates in the absence of electrostatic interaction at cmc and the coexistence of free DDAO micelles at high surfactant concentration. This behaviour may be ascribed to the non-ionic character of DDAO.

Acknowledgements

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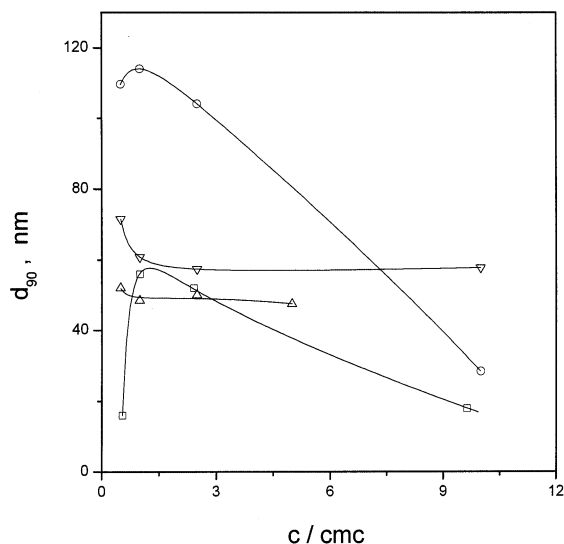


Fig. 4. Hydrodynamic diameter d_{90} of NaHA-surfactant mixture in 0.25 M NaCl versus ratio c/cmc . The surfactants used: \square 12-8-12, \circ DDAO, \triangle DTAB, and ∇ DC surfactant.

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