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ORIGINAL CONTRIBUTION

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Effect of electrolytes on the physicochemical behaviour of sodium dodecyl sulphate micelles

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Abstract The values of the critical micelle concentration (cmc) and the degree of electrolytic micelle dissociation, *a*, for sodium dodecyl sulphate (SDS) as a function of the concentrations of the electrolytes added, NaCl, KCl, NaF, $NaClO_4$, NH_4ClO_4, and $Mg(ClO_4)_2$, have been determined. The values of the SDS cmc have been shown to depend on the kind and concentration of the electrolyte cations. The electrolyte cations cause a decrease of the cmc in the following order: $Na^+ < NH_4^+ < K^+ < Mg^{2+}$. Moreover, *a* depends on the kind and concentration of the electrolyte added. The electrolyte anions have a much smaller effect on the values of *a* than the cations. The anions enhance *a* in the following order: $F^- > ClO_4^- > Cl^-$. The effect of different electrolyte cations on *a* is observed; moreover the values of *a* either increase or decrease with the electrolyte concentration. Other micellization parameters of SDS versus the concentration of the electrolytes added have been calculated.

Keywords Sodium dodecyl sulphate · Micellization parameters · Ion effect · Conductivity

Introduction

The interest in micellar systems stems from increasing possibilities of their application in pharmacy, cosmetic products and for different tasks related to environmental protection. Moreover, the field of polymer–surfactant system applications has been considerably extended by many types of polymers [1].

Despite much progress in recognition of the properties of micellar systems there are still ambiguities and discrepancies in their descriptions; therefore, a full recognition of the properties of surfactants in solutions and, in particular, the conditions in which the aggregation of molecules in micelles takes place is desired.

The aim of the study reported here was to determine the influence of the kind and concentration of an electrolyte on the physical and chemical properties of aqueous solutions of sodium dodecyl sulphate (SDS). The authors of the hitherto published works on the subject [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12] have investigated only the effect of NaCl on the course of micellization of SDS. As a continuation and extension of the previous studies we have studied the influence of the following electrolytes on the SDS micellization: NaCl, KCl, NaF, $NaClO_4$, NH_4ClO_4, and $Mg(ClO_4)_2$. We began with the determination of the critical micelle concentration (cmc) of SDS as a function of the concentration of the electrolyte added. Next the electrolytic dissociation of SDS micelles was investigated.

The degree of electrolytic dissociation, *a*, of SDS micelles in the presence of NaCl has been reported by many authors, however, there is no agreement as to the direction of the changes of this parameter as a function of the electrolyte concentration. Some authors assume that the degree of dissociation of SDS micelles does not depend on the concentration of NaCl [4, 5, 13], whereas others report it increases [2, 5] or decreases [3, 6] with increasing concentration of NaCl. These contradictory reports prompted us to check the problem and moreover to establish the behaviour of parameters characterizing the structure and physical and chemical properties of SDS solutions in the presence of different kinds of ions of the electrolyte added.

Experimental

Materials

The salts used, NaCl and KCl (P.P.H. Polish Chemical Reagents "POCH" Gliwice, all salts: p.a.), NaF (Reachim USSR, 99%), $NaClO_4$ (XENON Łódź, p.a.), NH_4ClO_4 (Johnson Matthey Alfa Products, 99%), and $Mg(ClO_4)_2$ (Merck, 92%), were recrystallized twice or three times from doubly distilled water. SDS (Merck; purity above 99%) was used without further purification.

Measurements

All the solutions were prepared with doubly distilled water, whose conductivity was 1.0 μScm^{-1}. Two solutions with a given concentration of a salt studied were prepared. In one of them, a weighed portion of SDS was dissolved so that the SDS concentration in the solution was 6.9×10^{-2} $moldm^{-3}$. The solution of SDS with a salt was added successively to the SDS-free salt solution; thus, the salt concentration remained constant during the experimental run. The conductivity of the resulting solution was measured successively.

The highest concentration of a given electrolyte studied was the threshold above which opalescence appeared or crystals were formed in a micellar solution.

The electric conductivities were measured at 25 °C and 1 kHz using a Wayne Kerr B905 automatic precision bridge and a conductometric bell-shaped cell, type OK.-0902P (cell constant: 74.8 m^{-1}).

Results and discussion

Electrolyte effect on cmc

The values of the cmc, obtained from the plots of conductivity versus surfactant concentration (Fig. 1), were determined from the intersection points of the lines above and below the corresponding breakpoints, as described earlier [13]. The values of the cmc determined by us for SDS with different concentrations of electrolytes are presented in Table 1. The resulting error in the determination of the cmc was estimated as $\pm 5 \times 10^{-5}$ $moldm^{-3}$. The values of the cmc obtained by us for SDS in NaCl solutions are found to be in good agreement with those reported earlier [2, 3, 7].

For each electrolyte studied we have plotted the dependence of the SDS cmc on the salt concentration. The empirical curves were fitted by the dependence

$$y = (a + bx)/(1 + cx), \tag{1}$$

where y is the cmc and x is the electrolyte concentration and these concentrations are expressed in moles per cubic decimetre. For NaCl, NaF and $NaClO_4$ the experimental results were fitted by one curve for which $a = 0.0078 \pm 0.0001$, $b = 0.0537 \pm 0.0087$, and $c = 72.00 \pm 4.55$ ($R^2 = 0.998$). For the other electrolytes the following values of the coefficients were obtained:

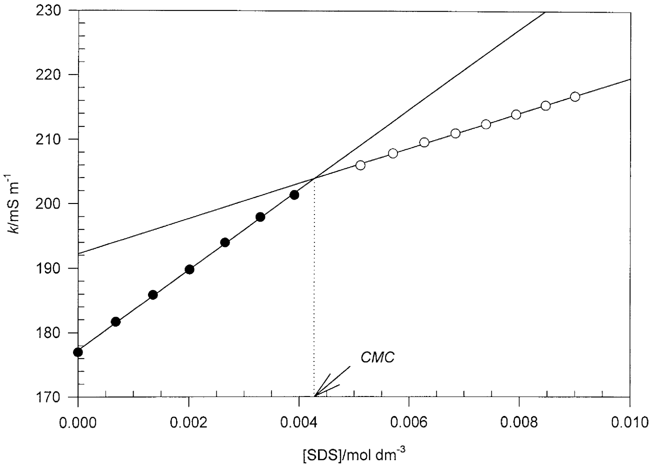

Fig. 1. Plot of specific conductivity of sodium dodecyl sulphate (*SDS*) in 0.015 $moldm^{-3}$ NaCl solution at 25 °C versus SDS concentration

$$NH_4ClO_4: \ a = 0.0078 \pm 0.0001, \ b = 0.0466 \pm 0.0139,$$
$$c = 95.45 \pm 8.47 \ (R^2 = 0.997)$$
$$KCL: \ a = 0.0079 \pm 0.0004, \ b = -0.258 \pm 0.074,$$
$$c = 82.34 \pm 36.65 \ (R^2 = 0.988)$$
$$Mg(ClO_4)_2: \ a = 0.0078 \pm 0.0001, \ b = 1.7441 \pm 0.2742,$$
$$c = 2088 \pm 193 \ (R^2 = 0.999)$$

Equation (1) enables us to calculate the values of the cmc for a given electrolyte concentration.

As already mentioned, for NaCl, NaF, and $NaClO_4$ the experimental results could be approximated by one curve, which means that the value of the cmc of SDS does not depend on the anions of the salts added. In the presence of the electrolytes with different cations the values of the SDS cmc decrease in the following order: $Na^+ < NH_4^+ < K^+ < Mg^{2+}$ (Fig. 2). This means that in the presence of Mg^{2+} ions the SDS cmc decrease is the greatest, while in the presence of Na^+ ions the SDS cmc decrease is the least.

Effect of electrolytes on *a*

The values of a were obtained from the ratio of the slopes of the lines above and below the cmc in the plots of the conductivity versus surfactant concentration (Fig. 1) as described earlier [1, 14]. The values of a determined by us for SDS micelles in the presence of the electrolytes studied at different concentrations are

Table 1. Values of micellization parameters of sodium dodecyl sulphate (*SDS*) for different concentrations of the electrolytes added at 25°C

Electrolyte	Electrolyte concentration (moldm^{-3})	Critical micelle concentration (moldm^{-3})	*a*	λ_0^- (Scm^{2}mol^{-1})	Λ_0 (Scm^{2}mol^{-1})	*Na*
With Na$^+$ cations. The values of *a* are given for NaCl	0.00	0.0078	0.42	118.0	66.27	21
	0.015	0.0042	0.435	141.5	62.33	27
	0.025	0.0033	0.445	154.1	58.60	30
	0.04	0.0026	0.45	166.5	60.87	33
	0.05	0.0023	0.46	176.2	62.19	36
	0.1	0.0017	0.68	292.9	52.89	63
	0.15	0.0014	0.62	284.2	79.75	63
	0.2	0.0012	0.6	289.2	84.91	66
	0.25	0.0011	0.49	244.6	293.9	57
	0.4	0.00098	0.25	135.0	272.9	33
NH_4ClO_4	0.00	0.0078	0.42	118.0	66.27	21
	0.015	0.0035	0.28	90.8	61.17	17
	0.025	0.0027	0.24	83.1	61.43	16
	0.04	0.0020	0.25	92.5	62.64	19
	0.05	0.0018	0.30	114.9	61.74	24
	0.07	0.0014	0.325	131.9	57.09	28
	0.1	0.0012	0.415	177.6	63.92	38
	0.15	0.0010	0.36	165.0	132.48	37
	0.2	0.0009	0.14	67.5	381.43	16
$Mg(ClO_4)_2$	0.00	0.0078	0.42	118.0	66.27	21
	0.0015	0.0025	0.575	143.5	65.08	24
	0.003	0.0018	0.355	90.7	64.57	15
	0.004	0.0016	0.225	59.3	61.56	10
	0.01	0.0012	0.125	37.0	59.11	7
	0.015	0.0011	0.155	48.8	69.52	9
	0.02	0.001	0.475	156.2	63.68	30
	0.025	0.00097	0.480	164.5	63.35	32
KCl	0.00	0.0078	0.42	118.0	66.27	21
	0.005	0.00505	0.45	131.6	64.45	23
	0.01	0.0025	0.13	39.5	62.51	7
	0.015	0.0018	0.22	70.0	59.89	13
	0.02	0.0012	0.38	126.3	61.00	24

presented in Table 1. As follows from the data in Figs. 3 and 4, the increase or decrease in *a* for SDS depends on the concentration range of the electrolyte added. This observed character of the changes in *a* for SDS can explain the differences between the literature data (see the Introduction).

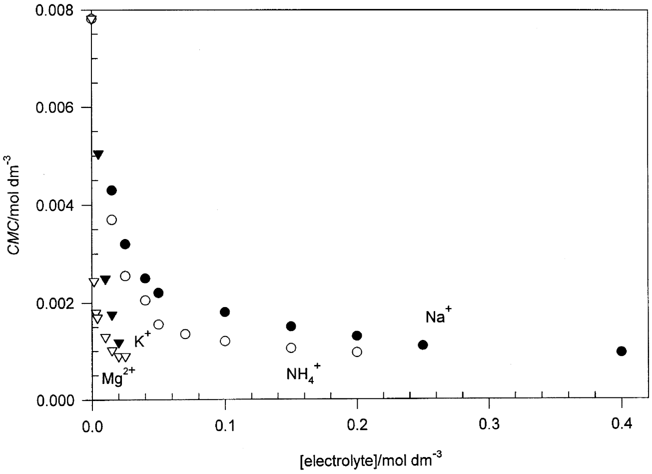

Fig. 2. Effect of the electrolytes added on the critical micelle concentration (*cmc*) for SDS at 25 °C

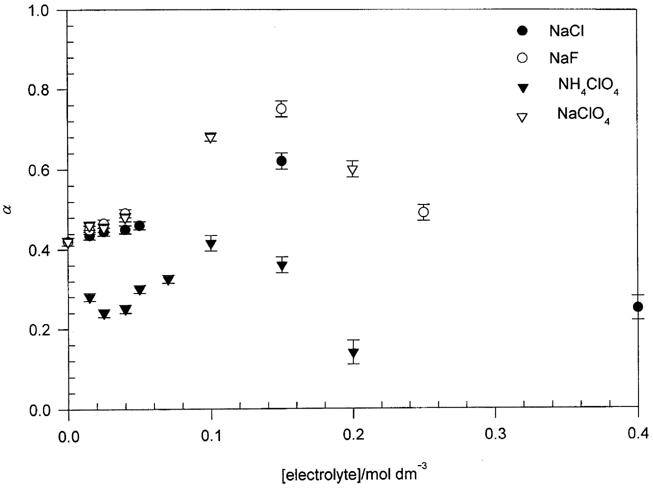

Fig. 3. Effect of ammonium and sodium electrolytes on the degree of electrolytic micelle dissociation, *a*, for SDS at 25 °C

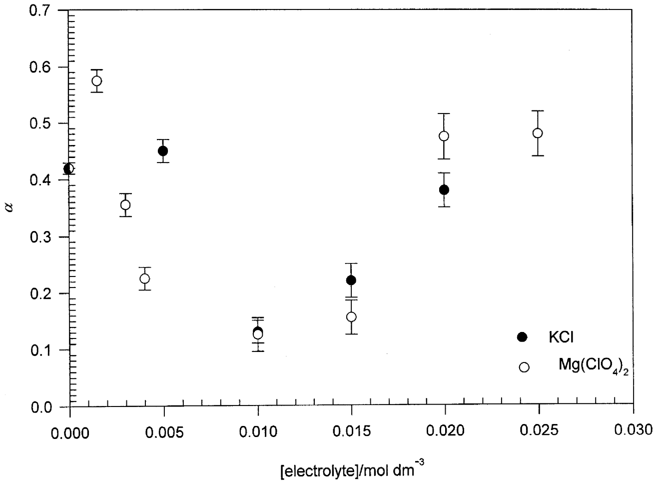

Fig. 4. Effect of KCl and $Mg(ClO_4)_2$ solutions on a for SDS at 25 °C

As follows from our results the values of a depend on the kind and concentration of the electrolyte added. The electrolyte anions cause a much smaller change in the values of a for SDS than the cations. The electrolyte anion effect on a is observed in the concentration range from 0 to 0.2 moldm^{-3} for NaCl, NaF, and $NaClO_4$ (Fig. 3). The anions cause an increase in a in the following order: $F^- > ClO_4^- > Cl^-$. The values of the electrolytic conductivity and the mean electrolyte activity coefficients of these electrolytes increase in the order $NaF < NaClO_4 < NaCl$, which can be explained in the following way. The greater the activity coefficients of an electrolyte, the smaller the interaction between its ions, which means that the electrolyte is more dissociated and its conductivity is higher. On the other hand, the smaller the activity coefficients of an electrolyte, the stronger the interaction between its ions, and the anions draw away Na^+ ions from the micelle surface of SDS in the order $F^- > ClO_4^- > Cl^-$, increasing the degree of electrolytic micelle dissociation. This effect is small because of small differences between the values of the electrolyte activity coefficients.

The different effect of particular electrolyte cations on the values of a is observed. We have observed three types of dependences of a on the electrolyte concentration. For the sodium electrolytes, the values of a at first increased, then reached a maximum and decreased (Fig. 3). For the ammonium electrolyte at the beginning, a decreased and having reached a minimum started changing as for the sodium electrolytes (Fig. 3). For the potassium and magnesium electrolytes, we observed two maxima separated by a minimum (Fig. 4).

A decrease in a observed for higher concentrations of sodium and ammonium electrolytes precedes the micellar transition from the spherical forms to rodlike ones, which according to Ref. [15] takes place at 0.4 moldm^{-3} Na^+ ions or 0.20–0.35 moldm^{-3} NH_4^+ ions. Besides, in aqueous solutions with high ionic strengths, a greater number of counterions bind to the micelle surface, causing a decrease in the degree of micelle dissociation [3].

The increase in a with increasing salt concentration can be explained either by increased charge screening at higher ionic strength [5] or by micelle growth in the presence of the electrolyte added. Such a growth of micelles would result in a decrease in the micelle charge density and, consequently, the liberation of counterions.

The decrease in a observed for KCl, $Mg(ClO_4)_2$, and in lower NH_4ClO_4 concentrations may be due to stronger interaction of SDS micelles with NH_4^+, K^+, and Mg^{2+} ions than with Na^+ ions. The NH_4^+ and K^+ ions are less hydrated than the Na^+ ions and, therefore, the NH_4^+ and K^+ charges are less screened than the Na^+ charges. The Mg^{2+} ions are the best hydrated among the ions studied here but their effective ionic charge is the greatest. Therefore, according to the effective ionic charge, the cations cause a decrease in a in the order $NH_4^+ < K^+ < Mg^{2+}$. The effective ionic charge of K^+ and Mg^{2+} is the greatest from among the cations studied, and probably that is why only for potassium and magnesium electrolytes the cationic effect on a appears already at very low electrolyte concentration (Fig. 4). It should also be noted here that in the presence of potassium and magnesium electrolytes, the values of the SDS cmc decrease especially drastically in comparison with the decrease in the cmc in the presence of sodium and ammonium electrolytes (Fig. 2).

Electrolyte effect on other micellization parameters of SDS

The values of the aggregation numbers, N, were obtained, following Refs. [4, 9, 10], from

$$N = K\left([\mathrm{Na}^+]_{\mathrm{aq}}\right)^{\gamma} \tag{2}$$

where $[Na^+]_{aq}$ is the molar concentration of Na^+ ions in the aqueous phase irrespective of whether it is provided by SDS or both SDS and added salt, and κ and γ are constants that depend only on the chain length of sodium alkyl sulphates [9]. The numerical values of κ and γ were estimated from experimental data and for SDS were found [4, 10] to be 164 and 0.25, respectively.

Equation (2) was derived from Huisman's empirical relationship [16] between the N and cmc.

The contributions to $[Na^+]_{aq}$ from the surfactant and the salt added can be found from the conventional pseudophase ion-exchange mass-balance relationship [10]:

$$[\mathrm{Na}^+]_{\mathrm{aq}} = a([\mathrm{SDS}] - [\mathrm{monomers}]) + [\mathrm{monomers}] + [\mathrm{Na}^+]_{\mathrm{ad}}$$
$$= a[\mathrm{SDS}] + (1-a)[\mathrm{monomers}] + [\mathrm{NaCl}], \qquad (3)$$

where [SDS] is the total molar SDS concentration, [monomers] is the molar concentration of the monomeric surfactant which equals the cmc, and $[\mathrm{Na}^+]_{\mathrm{ad}}$ is the molar concentration of Na^+ ions added.

Equation (2) in combination with Eq. (3) is a good empirical description of the experimental results [9]. Equation (2) no longer holds above the sphere-to-rod transition point [9].

In our work we have assumed that Eq. (3) may apply not only for Na^+ counterions but also for any univalent counterions. Then, we may rewrite Eq. (3) as follows:

$$[\mathrm{counterion}^+]\mathrm{aq} = a[\mathrm{SDS}] + (1-a)\mathrm{cmc} + [\mathrm{electrolyte}]. \qquad (4)$$

The values of N found from Eq. (2) in the presence of NaCl at the concentrations 0.0, 0.05, 0.1, 0.15, and 0.4 moldm^{-3} are in agreement with the literature data [3, 9, 10]. The values of N increase with increasing electrolyte concentration because the repulsive interactions between the head groups in the micelles decrease (the electrostatic screening effect).

If N and a are known, the charge, Na, and the radius, r, of the micelles can be calculated. Presuming the micelle to be spherical in shape, r is computed from the relation [2]

$$r = [3/(4\pi)(27.4 + 26.9n_{\mathrm{C}})N]^{1/3}, \qquad (5)$$

where n_{C} is the number of carbon atoms per hydrocarbon chain of the surfactant used and r obtained from Eq. (5) is given in angstroms. Similarly to the aggregation number, the radius of the micelle increases with increasing electrolyte concentration.

If the values of r are known, the surface area per head group, A_0, in the micelle can be calculated from [17]

$$A_0 = (3\upsilon)\Big/r\left(\text{Å}^2\right), \qquad (6)$$

where υ is the volume of the individual chain in the micelle and $\upsilon = 27.4 + 26.9n_{\mathrm{C}}$ (Å^3) [14]. The values of A_0 decrease with the concentration of electrolyte added.

We have also calculated the critical packing parameter, which controls the micellar shape [14]:

$$p_{\mathrm{m}} = \upsilon/(A_0 l). \qquad (7)$$

where l is the critical chain length and $l = 1.5 + 1.265n_{\mathrm{C}}$ (Å), and $p_{\mathrm{m}} = 0.33$ for spherical micelles, 0.5 for cylindrical micelles, and 1 for disks or bilayers. The packing of the SDS micelles increases with increasing electrolyte concentration; this means that larger spherical micelles are formed ($0.32 \le p_{\mathrm{m}} \le 0.44$).

Moreover, the volume per surfactant molecule in the polar shell of the spherical micelle, V_{p}, was computed from [9]

$$V_{\mathrm{p}} = [4\pi/(3N)]\left[\left(r + 5\ \text{Å}\right)^3 - r^3\right], \qquad (8)$$

where 5 Å is the thickness of the polar micelle shell. The values of V_{p} decrease with increasing concentration of the electrolyte added.

The effect of the electrolyte concentration on the SDS micellization parameters calculated from Eqs. (2), (5), (6), (7), and (8) is shown in Table 2.

We evaluated the limiting ionic equivalent conductivity for SDS micelles, λ_0^-, and the limiting equivalent conductivity of a surfactant solution, Λ_0, below the cmc. The values of λ_0^- and Λ_0 were determined for different concentrations of the electrolytes added and are tabulated in Table 1. The Stokes–Einstein relation [2] was used to estimate the values of λ_0^-:

$$\lambda_0^- = (Nae_0F)/(6\pi\eta r), \qquad (9)$$

where e_0 is the elementary charge, F is the Faraday constant, and η is the viscosity of water. At SDS concentrations below the cmc, the slopes of the conductivity versus SDS concentration plots represent the limiting equivalent conductivity (Λ_0) equal to the sum of the limiting equivalent conductivities of the indi-

Table 2. Values of N, r, A_0, p_{m}, and V_{p} of SDS micelles for different concentrations of NaCl at the critical micelle concentration and 25 °C

NaCl concentration (moldm^{-3})	N (Eq. 2)	r (Eq. 5) (Å)	A_0 (Eq. 6) (Å^2)	p_{m} (Eq. 7)	V_{p} (Eq. 8) (Å^3)
0.00	49	16.0	66	0.32	442
0.015	61	17.2	61	0.34	402
0.025	67	17.8	59	0.35	387
0.04	75	18.4	57	0.36	370
0.05	78	18.7	56	0.37	363
0.1	93	19.8	53	0.39	340
0.15	102	20.4	51	0.41	325
0.2	110	20.9	50	0.42	315
0.25	116	21.3	49	0.43	309
0.4	131	22.2	47	0.44	294

vidual ionic species present in a surfactant solution [1]. For each electrolyte studied, the values of λ_0^- of the SDS micelles change with the salt concentration because the charge (Na) of the micelles depends on the kind and the concentration of the electrolyte added. Hence, λ_0^- decreases and increases in the same ranges of the electrolyte concentration as a. For SDS micelle the value of λ_0^- is the greatest and the smallest in the presence of 0.1 moldm^{-3} NaCl and 0.01 moldm^{-3} $Mg(ClO_4)_2$, respectively.

Conclusions

The results of our study are the following.

1. The values of the SDS cmc decrease in the presence of electrolyte cations in the following order: $Na^+ < NH_4^+ < K^+ < Mg^{2+}$.
2. In some concentration ranges of the electrolyte added, the degree of electrolytic micelle dissociation can increase or decrease or be constant. Then, the degree of electrolytic micelle dissociation changes with the electrolyte concentration, which is in accordance with Eqs. (6) and (14) in Ref. [8]. These two equations imply that the actual degree of micelle dissociation changes with electrolyte concentration. In contradistinction to the former, the degrees of electrolytic micelle dissociation, based on the ideal case, are independent of the electrolyte concentration because it is assumed that the activity coefficients of individual species are unity [12].
3. The degree of electrolytic micelle dissociation depends on the kind of the electrolyte added. The cations of a given electrolyte are attracted by the negatively charged surface of SDS micelles, while the anions of this electrolyte are repulsed by it [15]. Therefore, the electrolyte anions cause a much smaller change in the values of a for negative micelles than the electrolyte cations. The anions cause an increase in a in the following order: $F^- > ClO_4^- > Cl^-$. The effect of different electrolyte cations on a is observed. The effect of different cations on a may be due to a change in the activity coefficients of the counterions, unmicellized coions, and micellar ions, because, if different counterions, i.e., Na^+ and other cations, are present in the surface region of SDS micellar solution, additional interionic interactions appear [8]. If the differences between Na^+ ions and other cations of the electrolyte added are greater, changes in the interionic interactions and activity coefficients of the individual species are also greater. Moreover, the salt cations and anions affect differently the water structure [18], which may also be responsible for the different character of electrolytic micelle dissociation in the presence of different electrolytes. Finally, one has to state that the electrolyte effect on a is a very complex one.
4. In our work the effect of the kind of electrolyte on SDS micellization is manifested by the cmc (Fig. 2) and a (Figs. 3, 4). Consequently, the aggregation number, N, does not depend on the kind of electrolyte added because in Eq. (2) (in combination with Eq. 3 or 4) the electrolyte concentration suppresses the effect of a on N: $a[\mathrm{SDS}] + (1-a)\mathrm{cmc} << [\mathrm{electrolyte}]$). The micellization parameters of SDS, r, A_0, p_m, and V_p, depend on N only, and do not depend on a (Eqs. 5, 6, 7, 8). Therefore, these parameters do not depend on the kind of electrolyte added. On the other hand, the micellization parameter of SDS, λ_0^-, depends on the kind of the electrolyte added because this parameter not only depends on N but also depends on a (Eq. 9).

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