

Water Activity in Aqueous Solutions of Inhomogeneous Electrolytes

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The activity of water in the bulk aqueous and surface regions of inhomogeneous solutions of electrolytes was determined by the method based on hydration of aldehydes. The inhomogeneous solutions of electrolytes used in the study were those of spherical and rodlike SDS micelles. It was established that in the bulk aqueous phase of the micellar SDS solution the change of the water properties was mainly determined by the anions of the electrolyte. Chloride and perchlorate ions were found to decrease the water activity. The change of water properties in the surface micellar phase of SDS solution is mainly determined by the cations of the electrolyte; sodium and ammonium ions decrease a_w , while potassium and magnesium ions increase it. From an analysis of the electrolyte concentration effect on the water activity the micellar sphere–rod transition has been estimated.

1. Introduction

The mechanisms of many chemical reactions taking place in homogeneous systems have been recognized and explained; therefore, the interest has shifted to the still unresolved processes occurring at the interfaces. The course of these processes depends significantly on the structure of the interface, so their explanation, and thus modification and control, require recognition of the properties of the interface.

A micellar system is an example of a system in which a chemical reaction can occur at the interface. Individual reagents, intermediates, and final products can be either separated in different regions of a micellar system (the core region, the surface region, the bulk aqueous region) or cumulated in one of them. Moreover, the interactions occurring in aqueous micellar solutions, i.e., attraction between hydrocarbon chains and repulsion caused by electrostatic or steric interactions among polar groups of surfactant molecules, are similar to the interactions stabilizing biological membranes and tertiary structure of proteins. Thanks to this similarity, micelles are used for modeling of different properties of more complex biological systems and processes taking place therein.^{1,2} Results of the studies on association and solvation of surfactant molecules and micelles in aqueous solutions can be helpful in understanding the role of water in the course of processes taking place in biological systems.³

The purpose of the reported in this paper study was to deepen of the recognition of the water properties in the surface region and the bulk aqueous region of a micellar system.

2. Experimental Section

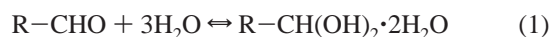
2.1. Reagents. The following reagents were used. Sodium chloride (NaCl), potassium chloride (KCl), and potassium fluoride (KF) were obtained from P.P.H. Polish Chemical Reagents "POCH" Gliwice (all salts: p.a.). Sodium fluoride (NaF) was from Reachim, USSR (99%). Sodium perchlorate (NaClO₄) was from XENON Łódź, (p.a.). Ammonium perchlorate (NH₄ClO₄) was from Johnson Matthey Alfa Products (99%).

Magnesium perchlorate (Mg(ClO₄)₂) (92%), sodium dodecyl sulfate (C₁₂H₂₅SO₄Na) (>99%), and propionaldehyde (C₃H₆O) (98% GC) were from MERCK. Caproaldehyde (C₆H₁₂O) was from Fluka AG (99% GC).

The salts were two or three times recrystallized from doubly distilled water; SDS was used without further purification. The aldehydes were distilled prior to use. The purity of aldehydes and their solubility was verified by a low value of absorbance measured at $\lambda = 230$ nm.

The weight portions of salts were dissolved in an aqueous micellar solution of 6.9×10^{-2} mol dm⁻³ sodium dodecyl sulfate (SDS). All solutions were prepared with doubly distilled water whose conductivity was $1.0 \mu\text{S cm}^{-1}$.

2.2. The Method. The water activity was determined on the basis of the reaction of the hydration of aldehydes. This method is described in detail in refs 4 and 5, so here it is presented very shortly. The reaction of hydration of aliphatic aldehydes catalyzed by H⁺ ions can be written as follows:



At a given temperature and pressure, the hydration equilibrium is described by the equilibrium constant K_H ,

$$K_H = \frac{a_D}{a_C a_W^3} = Q_H a_W^{-3} \quad (2)$$

where $Q_H = [D]/[C]$ and a_C , a_D , and a_W are the activities of the carbonyl form R-CHO (C), the gem-diol form R-CH(OH)_2 (D), and a water molecule (W), respectively.

The above formula holds assuming that the activity coefficients of C and D are the same, since the both forms occur at low concentrations and are not charged (the very small aldehyde concentrations used, 0.01–0.02 mol dm⁻³).

The ratio of the concentrations, $Q_H = [D]/[C]$, can be determined on the basis of spectrophotometric data from the equation

$$Q_H = \frac{A_0 - A_\infty}{A_\infty} \quad (3)$$

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where A_0 and A_∞ are the absorbances of the carbonyl form (C) at $\lambda_{\max} = 282$ nm measured directly after mixing the aldehyde with the solution (A_0 , for the time $t = 0$) and after reaching equilibrium between the carbonyl form (C) and the gem-diol form (D) (A_∞ , for the time $t \rightarrow \infty$).

This method allows determination of water activity not only in the bulk aqueous region but also in the surface region of the micelles. Long-chain aldehydes, such as hexanal, heptanal, or octanal, are poorly water soluble, and therefore in aqueous micellar solutions these aldehydes are usually placed in micelles. However, the measurements of absorbance indicate that the carbonyl groups are in an aqueous environment. For aliphatic aldehydes, the wavelength of the maximum absorbance (λ_{\max}) depends on the polarity of the solvent and can take values from 282 nm in water to 293 nm in nonpolar solvents (*n*-hexane).⁶ Therefore, if in micellar solutions for all aldehydes this wavelength (λ_{\max}) takes the value of 282 nm, the carbonyl groups cannot be placed within the core of the micelles whose structure and polarity are similar to those of liquid hydrocarbons. As follows from the above, in micellar solutions, long hydrocarbon chains of aliphatic aldehydes (starting from hexanal) are within the core of the micelles while the polar groups are in the surface region. Therefore, the hydration of aldehydes is determined by the properties of water in the surface region of the micelles.

To find Q_H , the absorbance was monitored from the moment of mixing of the aldehyde with the aqueous solution until the hydration equilibrium was reached. The measurements were conducted on a UV-vis spectrophotometer type "SPECORD M-40" made by CARL ZEISS JENA and equipped with an attachment for investigation of chemical kinetics stopped-flow type DIA-IUP, made by Dialog from Düsseldorf. The solutions were thermostated both prior to and during measurements.

As a result of addition of an aldehyde to a solution studied, the absorption band of the carbonyl group can be overlapped with the light scattered by the micellar solution, e.g., SDS micelles strongly scatter light of wavelengths shorter than 400 nm. To eliminate this effect, both cells placed in a spectrophotometer, the measuring one and the reference one, were filled with the micellar solution studied.

The results of the measurements were used to calculate Q_H , from eq 3, whereas the water activity was determined from eq 2. The values of K_H were obtained from the measurements performed for the system of butanol and water for which the water activity was known to be $a_w = 1$. The values of K_H are in agreement with those reported earlier⁴ within the limits of the error.

Measurements were conducted for propanal in the bulk aqueous region of micellar solutions and hexanal in the surface region of micelles

in the aldehyde concentration range 0.01 to 0.02 mol dm⁻³.

3. Results

The activity of water was first measured in micellar solutions with increasing content of SDS until the solution became more dense and gel-like. In solutions of concentrations above 0.9 mol dm⁻³ SDS, measurements were no longer possible. In the next stage, changes in the water properties in a micellar solution of 6.9×10^{-2} mol dm⁻³ SDS were studied as a function of concentration of the electrolyte added. The highest concentration of a given electrolyte in a micellar solution was the threshold above which measurements became inaccurate. In the solutions of NaCl, NaF, and NaClO₄ (sodium electrolytes) in concentrations higher than the threshold one, opalescence appeared, while

TABLE 1: Values of the Water Activity in Bulk Aqueous and Surface Regions of Micellar Solutions as a Function of SDS Concentration and the Electrolyte Concentration Effect on the Water Activity in the Micellar Regions of 0.069 mol dm⁻³ SDS Solution

electrolyte	concentration (<i>c</i>) mol dm ⁻³	water activity in SDS solutions in micellar region	
		bulk aqueous a_{wb}	surface a_{ws}
SDS	0.000	1.000	1.000
	0.069	0.970	0.882
	0.300	0.901	0.868
	0.450	0.866	0.847
	0.600	0.847	0.830
	0.800	0.827	0.823
NaCl	0.900	0.819	0.820
	0.00	0.970	0.882
	0.25	0.938	0.867
	0.40	0.931	0.817
	0.50	0.928	0.776
	0.75	0.926	0.767
KCl	0.00	0.970	0.882
	0.01	0.966	0.895
	0.02	0.964	0.906
	0.03	0.962	0.874
	0.04	0.961	0.843
	0.0	0.970	0.882
NaF	0.2	0.993	0.900
	0.3	1.001	0.916
	0.4	1.005	0.897
	0.5	1.002	0.854
	0.00	0.970	0.882
	0.02	0.975	0.898
KF	0.03	0.977	0.911
	0.04	0.978	0.893
	0.05	0.978	0.881
	0.06	0.977	0.870
	0.0	0.970	0.882
	0.1	0.941	0.873
NaClO ₄	0.2	0.928	0.864
	0.3	0.920	0.851
	0.4	0.917	0.818
	0.00	0.970	0.882
	0.20	0.929	0.875
	0.35	0.920	0.857
NH ₄ ClO ₄	0.50	0.913	0.852
	0.75	0.906	0.847
	0.000	0.970	0.882
	0.013	0.951	0.898
	0.025	0.941	0.904
	0.050	0.934	0.867
Mg(ClO ₄) ₂	0.065	0.933	0.857

in those with KCl and KF (potassium electrolytes), crystals precipitated. Highly concentrated solutions of NH₄ClO₄ showed opalescence and became viscous and dense of gel-like consistency, whereas in the solutions of magnesium perchlorate of concentrations higher than 0.065 mol dm⁻³ both opalescence and crystals appeared.

The values of the water activity in the bulk aqueous (a_{wb}) and surface (a_{ws}) regions of a micellar solution are given in Table 1: the temperature of measurements, 28 °C; the error in a_w determination, ± 0.01 . This table is the source of physical-chemical data of water activity in the presence of different electrolyte concentrations. For the sake of presentation, the dependence of a_w on electrolyte concentrations is also shown in Figures 1–3.

As a function of SDS concentration, the water activity in the bulk aqueous region decreases with increasing SDS amount (Figure 1); in the region of lower SDS concentrations, the decrease in a_{wb} is rapid, and at higher SDS concentrations it

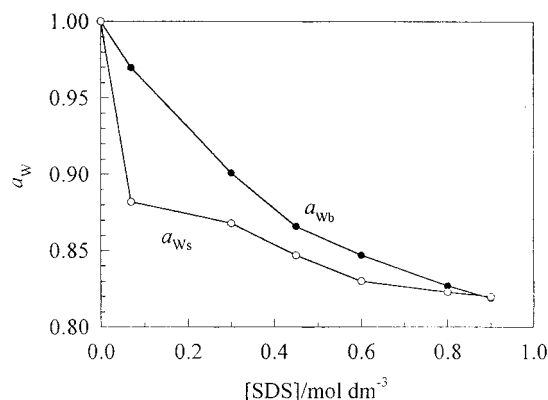


Figure 1. Dependence of the water activity in bulk aqueous, a_{wb} (●) and surface, a_{ws} (○) regions of micellar solutions on SDS concentration.

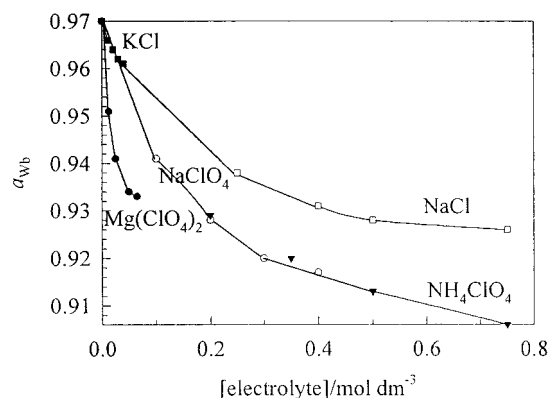


Figure 2. Dependence of the water activity in the bulk aqueous region (a_{wb}) of $0.069 \text{ mol dm}^{-3}$ SDS solution on electrolyte concentration for sodium (○), ammonium (▼), and magnesium (●) perchlorates and for sodium (□) and potassium (■) chlorides.

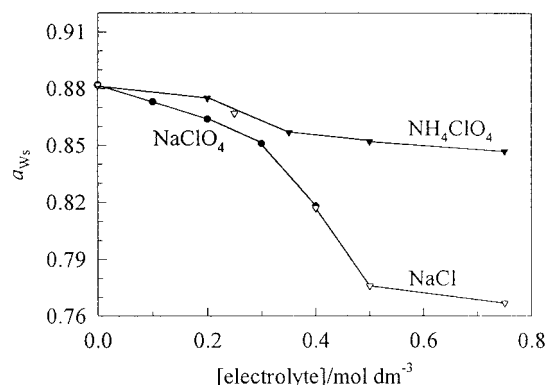


Figure 3. Dependence of the water activity in the surface region (a_{ws}) of $0.069 \text{ mol dm}^{-3}$ SDS solution on electrolyte concentration for sodium chloride (▽) and perchlorate (●) and for ammonium perchlorate (▼).

gets much slower. A similar change in the water activity in the bulk aqueous region of a micellar solution is observed as a function of electrolyte concentration in the presence of NaCl, KCl, NaClO₄, NH₄ClO₄, and Mg(ClO₄)₂ (Figure 2). For the fluorides studied NaF and KF, the electrolyte concentration dependence of the water activity shows different in the character. With increasing fluoride concentration, a_{wb} at first increases, in the beginning the increase is fast and later it slows down, and then slightly decreases (Table 1).

In the surface micellar region, the water activity, a_{ws} , rapidly decreases in the range of SDS concentrations growing from 0.0 to $0.069 \text{ mol dm}^{-3}$ SDS (Figure 1) and then slightly decreases to the concentration of 0.3 mol dm^{-3} and above this value its

decrease becomes rapid again. Above the concentration of 0.6 mol dm^{-3} , the water activity shows practically no changes.

In the surface micellar region, the water activity determined as a function of the electrolyte concentration behaves as follows.

(1) In the presence of NaCl, NaClO₄ or NH₄ClO₄ (Figure 3), it decreases with the increasing concentration of the electrolyte, and this decrease is small in the range of low concentrations and profound in the range of high concentrations,

(2) In the presence of KCl, KF, NaF, or Mg(ClO₄)₂ (Table 1) it increases in the range of low electrolyte concentrations and rapidly decreases in the range of high electrolyte concentrations.

4. Discussion

The properties of water, in both surface and bulk aqueous regions of a micellar solution with SDS at a constant concentration, change under the effect of electrolyte added. The cations of a given electrolyte are attracted by the negatively charged surface of SDS micelles⁷ while the anions of this electrolyte are repulsed by it. Therefore, the change in a_{ws} relative to the initial value in pure micellar solution of SDS (without electrolyte) can be assumed to be caused by the cation excess of a given electrolyte, whereas the analogous relative change in a_{wb} is caused by the anion excess of the electrolyte.

As far as the electrolyte concentration effect on the change of water properties in the bulk aqueous region of the SDS solution is concerned, its character (quantitative and qualitative) is similar for a given group of electrolytes, i.e., chlorides, fluorides, or perchlorates. This observation confirms the dominant role of the electrolyte anions in the bulk phase. On the basis of the experimental data (Table 1, Figure 2), we have observed that the fluoride ions cause an increase in the water activity while the chloride and perchloride ions cause its decrease. Moreover, the ClO₄[−] ions cause a much greater decrease in a_{wb} than Cl[−] ions. It is difficult to explain the increase in the water activity in the presence of fluorides on the basis of thermodynamics (Lewis–Randall, Gibbs–Duhem). At the present state of the research it is difficult to give a satisfactory explanation of the behavior of fluorides.

In analysis of the electrolyte concentration effect on the change of water properties in the surface region of SDS micelles we took into regard the range of the lowest concentrations of the electrolyte in which no rapid changes in a_{ws} were detected. For sodium chloride and perchlorate (Figure 3), the character of changes in the water activity is similar (a similar rate of a_{ws} decrease) which means that they are caused by the same factor, common Na⁺ cations present in the surface phase. The presence of ammonium ions decreases a_{ws} , however, to a lower degree than the presence of sodium ions (Figure 3) for the concentration range 0.0–0.2 mol dm^{−3}. For the solutions with sodium fluoride, we have assumed that apart from sodium ions also fluoride ions are present in the surface phase. Their presence can be explained as follows: F[−] ions are more strongly hydrated than Cl[−] or ClO₄[−],⁸ so their negative charge is more screened by surrounding water molecules. Consequently, part of the F[−] ions can approach the anionic micelle as a result of either thermal movements or self-diffusion and cause the change of the water properties in the surface phase. In the SDS solutions containing KCl and KF, we have observed that the presence of K⁺ ions causes an increase in a_{ws} (Table 1). It indicates the significant difference between Na⁺ and K⁺. The presence of magnesium ions was also found to lead to an increase in a_{ws} , see Table 1.

For all electrolytes studied, there is a special range of their concentration in which a rapid decrease of the water activity in

the surface phase of SDS micelles is observed. Such a jumpwise change in the water activity is most probably caused by a change in the properties of the micelle surfaces (the jumpwise change in a_{ws} only) and can be explained by the transition of spherical micelles into rodlike ones. Many authors have recognized such a transition by an abrupt change in a specific physical–chemical parameter (the mean hydrodynamic radius,^{9,10} the density and the molar volume of the hydrated micelle,¹¹ the viscosity,^{11,12} solubilization and surface tension measurements,¹² light scattering measurements,^{12,13} the aggregation number, and the second virial coefficient with osmotic pressure¹⁴).

For the sake of comparison, we studied changes in a_{ws} versus SDS concentration in the solutions without electrolytes (Figure 1). In the range of SDS concentrations from 0.0 to 0.069 mol dm⁻³, a significant decrease in a_{ws} is interpreted as due to formation of spherical micelles. With increasing SDS concentration from 0.3 to 0.6 mol dm⁻³, the water activity abruptly decreases which is interpreted as a consequence of the micellar transition from the spherical forms to rodlike ones. It is in consistence with Reiss–Husson et al.¹⁵ who reported this transition to occur starting from the concentration of 0.3 mol dm⁻³ SDS. At the concentrations 0.8 and 0.9 mol dm⁻³ SDS, the rodlike micelles are present and the value of a_{ws} is an almost constant.

In the bulk aqueous phase, the water activity decreases with increasing SDS concentration (Figure 1) to reach values comparable with a_{ws} at the concentrations 0.8 and 0.9 mol dm⁻³ SDS (Table 1). Such a profound decrease in the water activity can be caused by either a decrease in the water concentration or an increase in the ordering of the water structure in this bulk aqueous region.

The decrease of the water activity in the surface phase of spherical micelles is related to the increase in the degree of ordering of water molecules near the micellar surface.^{16,17} The even greater decrease in a_{ws} in the surface phase of rodlike micelles is explained as a result of a further increase in the degree of water molecule ordering¹⁸ and a decrease in the water concentration near the surface of the micelles (c_{ws}). The decrease in c_{ws} in the surface phase of rodlike micelles is a consequence of their partial dehydration.^{11,15,19} In contrast to the monomers of the ionic surfactant, the spherical micelles formed of them are not fully dissociated in water. The charge of ionic micelles is partly compensated by the counterions bound to the micellar surface.^{7,20,21} In the case of SDS micelles, the Na⁺ ions are bound to a micellar surface together with the hydrating water molecules that are also involved in hydrophilic hydration of the micellar surfaces.^{11,22} According to Ikeda,¹⁹ the degree of the rodlike SDS micellar dissociation ($\alpha = 0.79$) is much higher than that of the spherical SDS micelles ($\alpha = 0.39$). Therefore, as a result of the micellar sphere–rod transition, the number of Na⁺ ions decreases on the surface of the rodlike micelles.^{11,19} The Na⁺ ions are released from the surface of SDS rodlike micelles together with the hydrating water molecules which results in the above-mentioned partial dehydration of the rodlike micelles and the change in a_{ws} .

The detection of the rapid a_{ws} decrease followed by a constant value of this quantity was possible only for NaCl and NH₄ClO₄ (Figure 3). For high electrolyte concentrations, the SDS micelles are rodlike, which has been confirmed by the absorption spectra of the solutions containing 0.75 mol dm⁻³ NaCl or NH₄ClO₄ at 0.35 mol dm⁻³ to 0.75 mol dm⁻³. The intensity of the absorption signals recorded for these solutions is unproportionally high relative to that of the absorption signals of SDS

solutions with electrolytes at lower concentrations, which may indicate the presence of greater structures, large size micelles.

From the dependence of the water activity in the surface phase of SDS micelles on the concentration of an electrolyte, the concentration of the latter at which the transition of micelles from the spherical into rodlike occurs was determined. For NaCl, this transition takes place at 0.4 mol dm⁻³ NaCl, which is consistent with literature data obtained by other methods.^{9,12,13,19,23} At 25 °C, the spherical SDS micelles begin to transform into the rodlike ones in the solutions containing 0.40–0.45 mol dm⁻³ NaCl^{9,12,13,23} or higher concentration of NaCl.^{13,19} At the NaCl concentrations from 0.55 mol dm⁻³ to 0.80 mol dm⁻³, the SDS micelles are already rodlike.^{9,10,13,14,24} For the other electrolytes studied, the transition of the spherical into the rodlike ones takes place at about 0.04 mol dm⁻³ KCl, 0.40–0.45 mol dm⁻³ NaF, 0.04–0.05 mol dm⁻³ KF, about 0.4 mol dm⁻³ NaClO₄, 0.20–0.35 mol dm⁻³ NH₄ClO₄, and 0.04–0.05 mol dm⁻³ Mg(ClO₄)₂. As follows from the above, the transition of the spherical into the rodlike micelles of SDS occurs at the same amounts of NaCl, NaF, and NaClO₄ and the same amounts of KCl and KF. Moreover, the considerable visual changes in the solutions of the rodlike SDS micelles taking place under the effect of addition of a given electrolyte are characteristic for a given cation (compare the remarks on opalescence, appearance of crystals, or gel-like structures at the beginning of the Results section). Therefore, it can be concluded that in SDS micellar solutions the structural transition of micelles is stimulated by 0.4 mol dm⁻³ Na⁺ ions or 0.04 mol dm⁻³ K⁺ ions, 0.20–0.35 mol dm⁻³ NH₄⁺ ions or about 0.045 mol dm⁻³ Mg²⁺ ions. The tendency to the transition from the spherical to the rodlike SDS micellar structures increases in the presence of the cations in the following order: Na⁺ < NH₄⁺ < K⁺. A similar influence of electrolytes on the micellar sphere–rod transition has been observed by Nguyen et al.²⁵ using the calorimetric measurements. The series of cations promoting this micellar transition they found and the salt concentrations for NaCl, KCl, and NH₄Cl at which they observed the transition are in full agreement with our results.

In the SDS solutions without electrolytes, with increasing SDS concentration the spherical micelles grow to such a size that they are transformed into rodlike structures. This growth is possible thanks to a continuous attachment of SDS monomers, so from a given number of the spherical micelles much the same number of rodlike ones is formed. When to the solution of 0.069 mol dm⁻³ SDS we add an electrolyte at increasing concentrations, at a certain value of the latter the spherical micelles begin to join to one another (the salt effect). The absorption spectra of particular micellar solutions confirm that, with increasing concentration of an electrolyte, the micelles grow. Eventually, at a sufficiently high electrolyte concentration, the joined spherical micelles transform into the rodlike ones. Therefore, in this kind of solution, from a given number of the spherical micelles a much lower number of the rodlike ones are formed. In the SDS solutions with and without an electrolyte, the mechanisms of the rodlike micellar formation are different.

5. Conclusions

The activity of water in the bulk aqueous and surface regions of inhomogeneous solutions of electrolytes was determined by the method based on hydration of aldehydes. The inhomogeneous solutions of electrolytes used in the study were those of spherical and rodlike SDS micelles.

It was established that in the bulk aqueous phase of the micellar SDS solution the change of the water properties was

mainly determined by the anions of a given electrolyte. Chloride and perchlorate ions were found to decrease the water activity. The change of water properties in the surface phase of SDS solution is determined by the cations of a given electrolyte; sodium and ammonium ions decrease a_{ws} , while potassium and magnesium ions increase it.

From an analysis of the electrolyte concentration effect on the water activity, the micellar sphere-rod transition has been estimated. The above transition is manifested as a rapid (jumpwise) decrease in the water activity, a_{ws} , in the surface phase of the micelles. This abrupt change is interpreted as being due to an increase in water structure ordering around the micelles and a decrease in c_{ws} near their surface as a result of their partial dehydration. The tendency of SDS micelles to the transition from the spherical to rodlike structures increases in the presence of the cations, $\text{Na}^+ < \text{NH}_4^+ < \text{K}^+$, which is the order of decreasing ionic crystal radius.

In conclusion, it can be said that the method of aldehyde hydration is rather simple and effective for the determination of water activity in regions of micellar solutions and for the detection of the transition from the spherical into rodlike micelles.

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