Modified method of conductometric data analysis to calculate the conductivity of surfactant ions

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Abstract. Methodology for simple analytical refinement of the equivalent electrical conductivities of surfactant ions and counterions was proposed in the framework of the Debye – Hückel – Onsager theory as applied to surfactant dispersions at various concentrations. The developed methodology is based on the use of the mathematical form for the concentration dependencies of the specific conductivity in the premicellar region and makes it possible to calculate the equivalent conductivities of surfactant ions both under infinite dilution conditions and near the CMC. One of the advantages of the described method is the possibility of calculating the ion conductivities in the presence of a minimum number of experimental points (formally, a straight line can be constructed and its tangent of the angle of inclination can be determined even by two points corresponding to region 0.2 CMC — 0.8 CMC). Using the values of the equivalent conductivities of surfactant ions and counterions calculated for the required concentrations, allows to determine the parameters of the solution more accurately, including the contribution of micelles to the total conductivity of the solution.

1. Introduction

At the low (premicellar) concentrations of ionic surfactants, electrical conductivity of aqueous solutions is due to directed motion of charged particles, namely, surfactant ions and counterions. Accounting for the contribution of each type of charged particles is carried out using mobility $u_{\pm}$ charge carriers, or using molar or related equivalent electrical conductivities $\lambda_{\pm} = Fu_{\pm}$. For solutions of binary 1-1 electrolytes [1,2] the molar electrical conductivities of ions are identical with their equivalent electrical conductivities. The advantage of using equivalent (molar) electrical conductivities is the possibility of using tabular data relating to extremely dilute solutions, where the transfer of electricity is carried out by all ions independently from each other. The total molar conductivity of the solution under conditions of infinite dilution is a concentration of surfactants not less than CMC is requires. Therefore taking into account the real contribution of micelles to the solutions

equal to the sum of the molar conductivities of separate ions. At the infinite diluted solutions the equivalent electrical conductivities $\lambda_{\pm}$ increase to their limiting values λ_{0+} and λ_{0-} called the limiting equivalent electrical conductivities of ions. The limiting equivalent conductivities of ions are specific values for this type of ion. Their values at certain temperatures can be found in reference books for many types of ions [1,2].

At concentrations greater than the critical micelle concentration (CMC) the electrical conductivity is also determined by the contribution of micelles. To describe this contribution the mobility of micelles U_M which is proportional to their charge, and the related electrical conductivity $\lambda_M = FU_M$ of the micelles were introduced. It should be noted that for micelles the concept of the limiting equivalent conductivity cannot be introduced. At the infinite dilution micelles cannot appear. For their formation conductance requires the use of equivalent conductivity values for all types of charged particles under the conditions close to CMC.

A similar situation occurs when controlling the nanoparticles dispersing. When nanoparticles are dispersed in surfactant solutions, surfactant ions, which tend to association, form ordered structures on the phase's interfaces including the nanoparticle surfaces and prevent reagglomeration of nanoparticles. It is known that the most effective concentrations for dispersing nanoparticles such as carbon nanotubes are in the region close to CMC [3,4]. Therefore the characteristics of surfactant ions near the CMC are also required to control the occurring changes. The purpose of this work was to develop a simple analytical mechanism for refining the equivalent electrical conductivities of ions in the framework of the Debye – Hückel – Onsager theory with respect to surfactant dispersions at various concentrations. The developed mechanism is based on the use of the mathematical form the concentration dependences of the specific conductance in the premicellar region and makes it possible to calculate the equivalent conductivity of surfactant ions both under the infinite dilution conditions and near the CMC. Using the values of the equivalent conductivities of surfactant ions and counterions calculated for required concentrations allows one to determine the parameters of surfactant dispersions more accurately, including the micelle contribution to the total conductivity of solution. Numerical calculations are performed using the example of one of the most studied anionic surfactants - sodium dodecyl sulfate (SDS). The choice of this surfactant was dictated by our experience in studying SDS solutions [5,6] and phenomena occurring on the surfaces of carbon nanotubes dispersed in these solutions [7-9].

2. Method of calculating the limiting equivalent conductivities of surfactant ions according to conductometry data in the second approximation

In this paper we apply the method for determining the parameters of surfactant dispersions employing conductometric data, approximated by mathematical equations [10–15]. The approach and the experimental results taken as a basis are described in the article in the same issue [16]. For calculations we used the fact that for strong 1–1 electrolytes the dependence of electrical conductivity on the concentration expressed through mobility or equivalent conductivities of ions in the premicellar region has the form

$$\kappa(C) = F(u_+ + u_-) \cdot C = (\lambda_+ + \lambda_-) \cdot C = a \cdot C, \quad (1)$$

approximated by a straight line passing through the point $C = 0$. Here a is the tangent of the angle of inclination of line $\kappa(C)$ in the premicellar region which is determined from the experimental data. According to this equation, the equivalent electrical conductivities of ions are related by $a = \lambda_+ + \lambda_-$. In the first approximation the value of the equivalent conductivity of counterions λ_+ is replaced by a larger limiting value λ_{0+} , which may be found in the reference books. Accordingly, in this approximation the error is also included into the value of $\lambda_- = a - \lambda_{0+}$, which, on the contrary, is taken smaller than the real one.

On the face of it, in the first approximation according to the conductometric data for the value of the degree of ionization of micelles there is fairly good agreement with the experimental data (Part 1 of [16], table 1, string 2). However, a deeper analysis of the results indicates that in the first approximation there are discrepancies of the values of the equivalent conductivity of SDS ions λ_- with the literature data. The values of the limiting equivalent conductivity of SDS ions λ_{0-} found as a result of more accurate calculations, as expected, are usually somewhat higher [17, 18].

We decided to clarify the results obtained in the above calculations using the limiting law of ion conductance — a calculation equation describing the decrease in the equivalent electrical conductivity in the second approximation of the Debye – Hückel – Onsager theory [1,2]. The Debye – Hückel – Onsager theory makes it possible to determine experimentally the quantities characterizing infinitely diluted solutions, which can already be compared with the available reference data. The two points should be noted: a) there are several record forms for formula connecting λ_{0-} and λ_- [1,2]; b) whatever formula we take the calculations will still be approximate. Therefore we used one more approximation to develop an analytical method for calculating equivalent conductivity.

Our analysis of the literature data showed that in fact approximation is applied in the concentration region corresponding to 0.2 CMC - 0.8 CMC, and not for the initial region of the concentration dependence of conductivity corresponding to extremely dilute solutions (where ion mobilities do not depend on the concentration and such an approximation could be quite appropriate). With surfactant concentration increase the interaction of ions with each other increases, which leads to a decrease in the speeds of their movement and, consequently, to their contribution to the solution conductance. At the end of this section a decline due to the association of molecules into dimers and

into micelles begins. For this reason we assumed that the coefficient a , associated with the conductivities by relation (1), corresponds to a segment approximately located near 0.6 CMC. For sodium dodecyl sulfate at both temperatures, this roughly corresponds to a concentration of 5 mM. To consider the selected value with greater accuracy does not make sense.

According to the second approximation of the Debye – Hückel – Onsager theory a decrease in the equivalent conductivity when going from an infinitely diluted solution to solutions of final concentration is associated with the appearance of relaxation and electrophoretic effects of ion retardation [1]. The relaxation effect of ion retardation is due to the fact that the movement of an ion in an electric field leads to the asymmetry of the ionic atmosphere due to appearance of excess charges of the opposite sign behind the moving ion and to the emergence of additional electrostatic forces. The electrophoretic effect of ion retardation arises due to the fact that the ionic atmosphere of the central ion having a charge with an opposite sign moves under the action of an applied electric field in the reverse direction to the central ion. Therefore, the central ion does not move in a stationary medium, but in a medium moving towards it, which creates an additional effect of ion retardation. In addition, the introduction of the effective average ionic diameter d allows one to account for the intrinsic dimensions of the ions.

Taking into account all these factors allowed to derive a calculation equation describing the decrease in the equivalent conductivity of the solution (due to ions of both signs) as the ionic strength of solution I increases in the second approximation of the Debye – Hückel – Onsager theory:

$$\lambda_{\pm} = \lambda_{0\pm} - [B_1\lambda_{0\pm} + B_2] \cdot I^{1/2} \cdot (1 + Bd \cdot I^{1/2})^{-1} \quad (2)$$

Here $\lambda_{0\pm} = \lambda_{0+} + \lambda_{0-}$, $\lambda_{\pm} = \lambda_{+} + \lambda_{-} = a$ is denoted. The coefficient $B = (2e^2 \cdot N_A / \epsilon \cdot k \cdot T)^{1/2}$, besides the main physical constants, is determined by the dielectric constant of the medium and its temperature. The explicit form of the coefficients B_1 and B_2 , which characterize the relaxation and electrophoretic effects, respectively, are given in reference books, for example, in [1,2]. These coefficients depend on the dielectric constant of the medium, the viscosity of the solvent and the temperature. In ionic surfactants solutions in the premicellar region, the ionic strength is identical to concentration, i.e. $I = C$. For a binary solution of 1-1 electrolyte limiting law of ion conductance reduces to a simpler form [1]

$$\lambda_{\pm} = \lambda_{0\pm} - [0.2593 \cdot 10^5 \cdot (\epsilon \cdot T)^{-3/2} \cdot \lambda_{0\pm} + 0.2603 \cdot 10^{-4} \cdot (\epsilon \cdot T)^{-1/2} \cdot \eta^{-1}] \cdot C^{1/2} \quad (3)$$

Here all values are taken in the SI system. The Debye – Hückel – Onsager theory describes quite well the experimental data in dilute solutions (up to concentrations of 20 mM for SDS). However, not all factors leading to a discrepancy with experience were taken into account. There are more complex equations that allow to increase the accuracy of the calculation and to achieve greater agreement with the experiment, which is not always justified, since it requires the introduction of a certain number of adjustable parameters. The substitution of the relevant data, namely: $\epsilon = 78.25$, $\eta = 0.891 \text{ mPa} \cdot \text{s}$ ($T = 298 \text{ K}$) and $\eta = 0.653 \text{ mPa} \cdot \text{s}$ ($T = 313 \text{ K}$) allowed to write down equation (3) in a simpler form with numerical coefficients, and taking into account the concrete concentration $C = 5 \text{ mM}$ allowed us to further simplify the resulting ratio (numerical values of λ are taken in SI in of $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ units, concentration C is taken in $\text{B mM} = \text{mol} \cdot \text{m}^{-3}$).

$$T = 25 \text{ }^\circ\text{C}: \lambda_{\pm} = \lambda_{0\pm} - (0.00728 \lambda_{0\pm} + 1.913 \cdot 10^{-4}) \cdot C^{1/2} = 0.984(\lambda_{0+} + \lambda_{0-}) - 4.28 \cdot 10^{-4} = a,$$

$$T = 40 \text{ }^\circ\text{C}: \lambda_{\pm} = \lambda_{0\pm} - (0.00676 \lambda_{0\pm} + 2.547 \cdot 10^{-4}) \cdot C^{1/2} = 0.985(\lambda_{0+} + \lambda_{0-}) - 5.70 \cdot 10^{-4} = a. \quad (4)$$

These relationships with accounting of the numerical values of the coefficients a and the tabular values λ_{0+} , namely: $a = 66.7 \cdot 10^{-4} \text{ S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ [11], $\lambda_{0+} = 50.1 \cdot 10^{-4} \text{ S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ (for $T = 25 \text{ }^\circ\text{C}$), $a = 89.5 \cdot 10^{-4} \text{ S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ [12], $\lambda_{0+} = 67.6 \cdot 10^{-4} \text{ S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ (for $T = 40 \text{ }^\circ\text{C}$), made it possible to calculate the limiting equivalent electrical conductivity of the whole solution $\lambda_{0\pm}$ and surfactant ions λ_{0-} for both temperatures (also in $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$)

$$T = 25 \text{ }^\circ\text{C} \lambda_{0\pm} = 72.1 \cdot 10^{-4}, \lambda_{+} = 16.6 \cdot 10^{-4}, \lambda_{0-} = 22.0 \cdot 10^{-4}, T = 40 \text{ }^\circ\text{C} \lambda_{0\pm} = 96.5 \cdot 10^{-4}, \lambda_{+} = 21.9 \cdot 10^{-4}, \lambda_{0-} = 28.9 \cdot 10^{-4} \quad (5)$$

The values of equivalent electrical conductivities $\lambda_{-} = a - \lambda_{0+}$ at the same temperatures, obtained from conductometric data in the first approximation, are also given in relations (5). A comparison of the obtained numerical values allows one to notice a significant (by more than 20%) difference in the limiting equivalent electrical conductivities of SDS ions λ_{0-} calculated in the second approximation compared to their values in the first approximation λ_{-} . Despite such large discrepancies, the results obtained are in good

agreement with the literature data. The value $\lambda_{0-} = 21.49 \cdot 10^{-4} \text{ S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ for $T = 25^\circ \text{C}$ was obtained in [17] as a result of linear regression of experimental data (according to an earlier source $\lambda_{0-} = 24 \cdot 10^{-4} \text{ S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ at the same temperature [18]). A fairly good agreement of the results obtained by the method developed by us as well as the simplicity of its calculation should be noted.

We did not find the literature data on the values of the limiting equivalent conductivities of SDS ions for 40°C , but the calculated value $\lambda_{0+} = 28.9 \cdot 10^{-4} \text{ S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ is in good agreement with the known fact of an increase in electrical conductivities by 2% with a temperature increase by one Kelvin.

3. Calculation of the degree of micelle ionization in the second approximation of the Debye – Hückel – Onzager theory

The presence of data on the limiting conductivities of surfactant ions would seem to allow using the relations (5) to calculate the electrical conductivity of micelles. However, the formation of micelles is not associated with extremely low concentrations of electrolyte, and therefore the direct use of the calculated values to determine the parameters of micelles is unacceptable. To correctly account for the micelles contribution to the solution conductivity it is necessary to calculate the electrical conductivity of the surfactant ions at the micellization concentration, i.e. at CMC. Calculations for concentrations greater than the CMC don't make much sense, since the concentration of ions in diffuse shells of micelles increases slowly (mainly due to an increase in the counterions concentration). After micellization the contributions of free surfactant and its counterions remain constant and approximately equal to the CMC, the contribution of free counterions in the region near the CMC grows slightly with increasing the difference in concentration ($C - C_{\text{CMC}}$). The micelle concentration is generally very small, since the number of structural units decreases sharply during the aggregation of ions into micelle. The effects of changing the shape of micelles will be much stronger with increase in concentration. To determine the specific contribution of SDS ions to conductivity, we decided to use the fact that, according to the law (3), the concentration dependence of conductivities of ions of different signs has the same character.

This means that the proportions of the contributions should remain about the same as for infinite dilution when $\lambda_{0\pm} = \lambda_{0+} + \lambda_{0-}$. Thus for SDS

ions they should be 30.5 % at $T = 25^\circ \text{C}$ and 29.9 % at $T = 40^\circ \text{C}$ of the total conductivity $\lambda_{\pm} = \lambda_{+} + \lambda_{-}$ at other concentrations. Since in the region near the CMC $\lambda_{\pm} = a$, the calculation of the equivalent conductivities of surfactant ions and counterions with CMC gives the following values (in $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$):

$$T = 25^\circ \text{C}: \lambda_{\pm} = a = 66.7 \cdot 10^{-4}, \lambda_{+} = 46.4 \cdot 10^{-4}, \lambda_{-} = 20.3 \cdot 10^{-4},$$

$$T = 40^\circ \text{C}: \lambda_{\pm} = a = 89.5 \cdot 10^{-4}, \lambda_{+} = 62.7 \cdot 10^{-4}, \lambda_{-} = 26.8 \cdot 10^{-4} \quad (6)$$

The obtained values in the presence of data on the aggregation number of ions in the micelle N allow to calculate by the Evans formula [11,19]

$$\alpha = [-\lambda_{+} + (\lambda_{+}^2 + 4 \cdot \lambda_{-} \cdot b \cdot N^{2/3})^{1/2}] (2 \cdot \lambda_{-} \cdot N^{2/3})^{-1} \quad (7)$$

and by other formulae given in part 1 of this article, in particular,

$$\lambda_M = \alpha \cdot \lambda_{-} \cdot N^{2/3} \quad (8)$$

the degree of micelle ionization α and the micelle conductivities

$T = 25^\circ \text{C}$:

$$\alpha = 0.222, \lambda_M = 72.1 \cdot 10^{-4} \text{ S} \cdot \text{m}^2 \cdot \text{mol}^{-1}, T = 40^\circ \text{C}: \alpha = 0.232, \lambda_M = 92.1 \cdot 10^{-4} \text{ S} \cdot \text{m}^2 \cdot \text{mol}^{-1} \quad (9)$$

The use of the limiting law revealed a very good agreement of the results related to SDS ions. However the results for the degree of micelle ionization α (9), in our opinion, turned out to be slightly underestimated, and for conductivities of micelles, on the contrary, slightly overestimated. It would seem that the more rigorous calculation we carried out should improve the value of the degree of ionization of micelles and bring the results closer to the value $\alpha = 0.25$ and even a little more obtained in the course of various experiments [20-23]. But in this case this did not happen.

This discrepancy caused us to conclude that the assumptions used in the derivation of the Evans formula (7) are somewhat incorrect and to suggest other versions of the formulae for calculating the degree of micelle ionization. In particular, the use of the value of the radius of micelles allowed us to write the ratio derived in accordance with the methodology described in [16]. In relation to SDS, the adjusted ratios have allowed us to obtain micelle conductivity values differing by about 15%. However, the results obtained for M indicate that the contribution of micelles to the total conductivity of the solution cannot be neglected. Such a contribution is due to the fact that although micelle is a big formation compared with ion, but its

movement is associated with the transfer of a sufficiently large charge (approximately $15e$).

4. Conclusion

Thus, we have proposed a methodology for simple analytical refinement of the equivalent conductivities of surfactant ions and counterions in the framework of the Debye – Hückel – Onsager theory as applied to surfactant dispersions at various concentrations. The developed methodology is based on the use of the mathematical form for the concentration dependencies of the specific conductivity in premicellar region and makes it possible to calculate the equivalent electrical conductivity of surfactant ions both under infinite dilution conditions and near the CMC. One of the advantages of the described method is the possibility of calculating the conductivities of ions in the presence of a minimum number of experimental points (formally, a straight line can be constructed and its tangent of the angle of inclination can be determined even by two points corresponding to the 0.2 KKM area — 0.8 KKM). Using the values of the equivalent conductivities of surfactant ions and counterions calculated for the required concentrations, allows to determine the parameters of solution more accurately, including the contribution of micelles to the total conductivity of the solution.

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