CONDUCTANCE FLUCTUATION SPECTROSCOPY OF MICELLAR SOLUTIONS IN FLOW

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In [1] the method for measurements of large-scale conductance fluctuations in a flow was developed and its applicability to analysis of ultradisperse systems was demonstrated. It was shown that the minimum size of colloid particles at which their contribution to the spectrum of solution conductance fluctuations is still resolvable is about 10 *nm*. This value is known to be the size of micelles of various classes of surfactants. Here we report the results of the studies on conductance fluctuations of water-salt surfactant solutions for medium and high concentrations of isotropic micellar solutions. The objects were H_2O—NaCl — sodium dodecyl sulphate (SDS) system in the region of an isotropic solution of rodlike micelles and H_2O—NaCl — eycosanethylene glycol octadecyl monoether ($C_{18}E_{20}$) system, with near-spherical micelles over a wide range of concentrations. The measured quantity was the fluctuations in conductance of a quartz 26 μm diameter and 408 μm length capillary filled with the investigated solution, with the solution flow maintained by hydrostatic pressure drop $1.4 \cdot 10^3$ *Pa*.

In the case of nonionic surfactant one can assume the dependence of conductance fluctuations on micellar parameters to be the same as for suspension of noninteracting spherical non-conducting particles in an electrolyte solution [1]. For micelles of diameter d_0 and aggregation number m_0 the relative mean square fluctuation for surfactant concentration well above the cmc is proportional to d_0^6 / m_0 and so can be the basis for determining micellar size. Figure 1 represents values of mean square conductance fluctuation calculated by integration of spectra in solutions of $C_{18}E_{20}$ in 1.25 *M* NaCl. The experimental data are satisfactorily approximated by theoretical curve at the values of aggregation number m_0=100 and micelle diameter 9.1 ± 0.6 *nm*, which is close to the double length of $C_{18}E_{20}$ molecule.

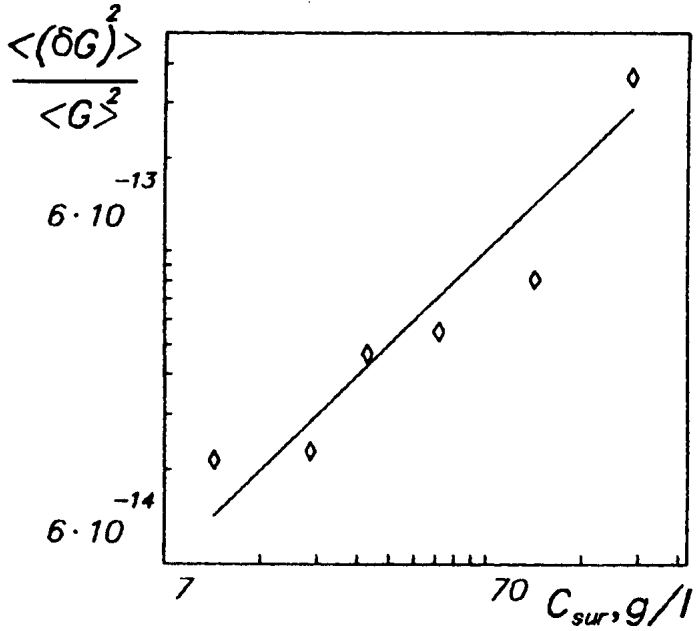

Fig.1. $\langle(\delta G)^2\rangle / \langle G\rangle^2$ *vs.* surfactant concentration for $C_{18}E_{20}$ — 1.25 *M* NaCl system at 50° *C*. Straight line — theoretical dependence at $m_0 = 100$ and $d_0 = 9.1$ *nm*

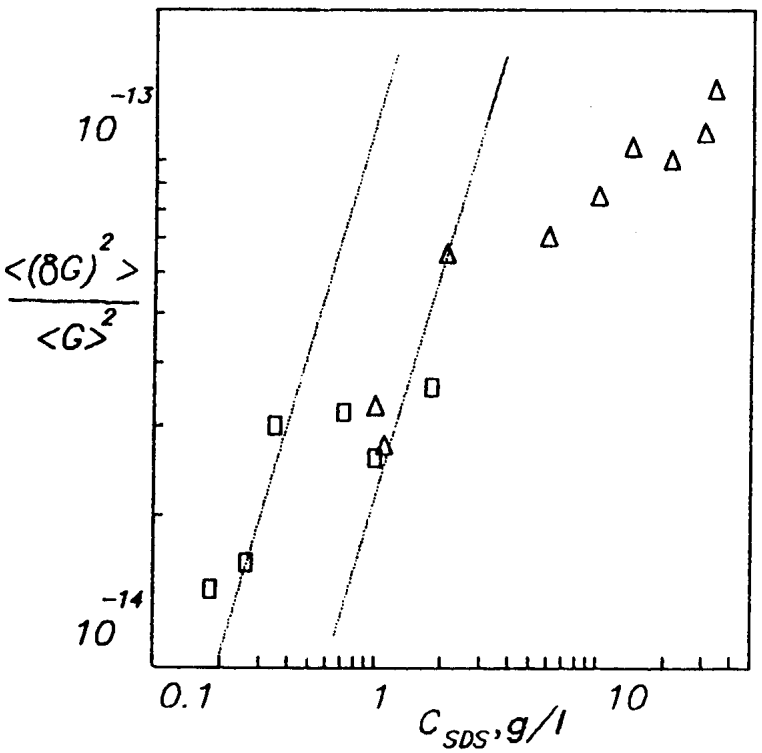

Fig.2. $\langle(\delta G)^2\rangle / \langle G\rangle^2$ *vs* surfactant concentration for SDS— NaCl— H2O system at 40° *C* for 1.0 *M* (Π) and 1.25 *M* NaCl (V) concentrations. Dached lines — theoretical dependence for these salt concentrations

In the case of ionic surfactant SDS in solution of high ionic strength the contribution of the Coulomb interaction of SDS micelles to the mean square fluctuation of their concentration is negligible, and thus we can regard micelles to be uncharged. For rodlike micelles with a polydisperse size distribution [2] one can obtain the expression for mean square conductance fluctuation that connects it with parameters of the distribution. The concentration dependence of $\langle(\delta G)^2\rangle / \langle G\rangle^2$ is given in fig.2. At low surfactant concentrations, the dependence of conductance fluctuations on SDS concentration is close to the theoretical one, and the estimate of micelle size distribution parameters for 1 *M* NaCl obtained from these findings is close to the value resulting from light scattering data [3]. As the surfactant concentration increases the values of $\langle(\delta G)^2\rangle / \langle G\rangle^2$ tend to be smaller than those calculated from theory, which appears to be evidence of a noticeable spatial correlation

of micelles. We can show that neither Coulomb nor steric (rotational overlap) interactions are able to be the reason for such a great decrease of fluctuation level. But the polyelectrolyte behaviour of micelle might, in principle, smooth the conductance jump during its passage through the capillary. For a spherical micelle we obtain about 10% compensation of the small ion "ousting" effect by polyelectrolyte behaviour of the micelle. This compensation grows as micelle size increases [4]. Such estimations permit us to conclude that polyelectrolyte properties of SDS micellar solutions are the most probable reason of the fluctuation reduction at high surfactant concentrations.

References

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