Strongly Correlated Electronic States in Aqueous Micellar Surfactant

Yuri Mirgorod (✉ storogenko_s@mail.ru)

Southwest State University

Research Article

Keywords: strongly correlated electronic systems, water, surfactants, micelles, thermal fluctuations, quantum fluctuations

Posted Date: June 30th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-660013/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Strongly correlated electronic states in aqueous micellar surfactant systems

Mirgorod Yu. A.

Southwest State University

Kursk, Russia

yu_mirgorod@mail.ru, storogenko_s@mail.ru

Abstract

Strongly correlated electronic states (SCES), that determine the anomalies of physicochemical properties, are well-known for solid materials at low temperatures. According to the mechanism of manifestation their existence can be assumed in biological cells with white spots, which makes us look into this challenging problem in detail. The paper presents its solution through a study of simple models of micellar solutions of ionic surfactants. The process of micelle formation with accompanying liquid-liquid phase transition makes us pay attention to possible anomalies of properties. Therefore the SCES of water micellar solution has been tested by compension and cooperative effects; and by small-angle, wide-angle X-ray, dynamic and chiral scattering of electromagnetic radiation. The solution water is represented by ensembles of small nano systems. Therefore, thermal (cavities for micelles 2-6 nm) and quantum (0.2-0.3 nm) fluctuations of water appear in the zone of concentration of micelle formation. Their energy is approximately equal to the H-bond. Contraction (expansion) of water H-bonds network of due to quantum fluctuations on a small scale correlates with the expansion (contraction) of the in the cavities in the micelles H-bonds network due to thermal fluctuations on a large scale. This phenomenon is caused by SCES.

Key words: strongly correlated electronic systems, water, surfactants, micelles, thermal fluctuations, quantum fluctuations

Introduction

Solid materials with SCES develop completely new phenomena and functions in: the Mott transition, high-temperature superconductivity, topological superconductivity, colossal magnetoresistance, and giant magnetoelectric effect [1]. Emergent properties of solid materials appeared at low temperatures.

The situation is opposite for aqueous solutions of surfactants. The emergent properties of aqueous surfactant solutions (micelle formation, solubilization) are perceived as ordinary, because they were opened long ago. Among other things micelles are used as models for studying processes occurring in protein solutions, cells, viruses [2] and for patients' treatment [3].

The present paper is the only one where quantum properties of these colloidal systems have been demonstrated and proved. Therefore, SCES technologies are not yet used for the treatment of diseases, in technology, or we may just not know anything about their use.

At present, there is a lot of skepticism about the appearance of aqueous SCES at room temperature due to the fact that quantum phase transitions and quantum materials have so far been obtained at low temperatures.

Researchers armed with their calculation, spectroscopy, and the isotope effect means are intensively forcing their way to understanding the participation of quantum fluctuations (ZPE) in the formation of the properties of water. They do it in order to understand how important it is to take into account the contribution of ZPE to explain the properties of water. ZPE can be thought of as a sum of three components that are contributions to ZPE from O-H stretch modes (ZPES), H-O-H bending modes (ZPEB), and torsional modes (ZPET).

For polyhedral clusters $(H_2O)_n$ $n = 8-20$, the calculation revealed a close correlation between ZPE and the electronic energy of the cluster in the ground state E_0 . Each increase in E_0 by 1 kcal/mol corresponds to a decrease in ZPE by 0.11 kcal / mol. ZPEB does not correlate with E_0 , while ZPES is correlated positively and ZPET is negative. ZPES and ZPET correlate strongly with each other [4].

In our search for search for SCES, the last conclusion about water directs us to micellar surfactant solutions and here's the reason. Micelle formation is accompanied by a liquid-liquid phase transition in an ensemble of small water systems [5]. Small water systems are equal to the volume of surfactant molecules and therefore their extensive thermodynamic functions fluctuate up to 50%. Near the critical micelle concentration (CMC) or the midpoint of the liquid-liquid phase transition, the electron densities of thermal and quantum fluctuations come to the fore.

They determine the formation of topological defects and the growth rate of correlated regions of water and surfactants. In this paper in order to determine the secrets of this new phenomenon we test SCES with various methods: compensation, cooperative effects, low angle, wide angle X-ray, dynamic and chiral scattering

Results

1. Compensation effect

We tested the following selected systems for the existence of SCES in them by our original method of the compensation effect. It is a compensation for changes in the enthalpy ΔH_i and entropy ΔS_i of similar processes that are observed during the dissolution of organic compounds, micelle formation of surfactants, or proteins with a change in temperature or volume (the length of hydrocarbon radical)

$$\Delta H_i = \Delta H_{T=0} + T_c \Delta S_i, \quad (1)$$

where T_c – is the iso-equilibrium temperature, and $\Delta H_{T=0}$ – is constant, The nature of the phenomena described by equation (1) has not been clarified, and the authors of the review on this topic [6] considered such equations to be mysterious.

For a series of 8 liquid n-hydrocarbons with the presented units of measurement at 298K, we obtained

$$\Delta H_i = 273 \cdot \Delta S_i + 22,48 \text{ kJ/mol of hydrocarbon} \quad (2)$$

$$\Delta H_i = 273 \cdot \Delta S_i + 22,48 \text{ kJ/mol of OH bond H}_2\text{O} \quad (3)$$

It can be seen from equations (2), (3) that the process of dissolution of hydrocarbons in water (phase transition in an ensemble of small water systems) at 298K and phase transition in water at 273K are the same phenomenon. They are accompanied by the same enthalpy change of 4.9 kJ/mol, but they have different phase transition temperatures. This conclusion was confirmed by another method [5]. In equation (3), the value of 22.48 kJ/mol of O-H bonds of water coincides with the value of ZPE of water [7], since at $T = 0\text{K}$ $\Delta S_i = 0$.

The interchange of the names of the units of measurement $\Delta H_{T=0}$ in equations (2) and (3) is possible due to approximately the same values of ZPE $\text{CH}_2 = 23.03$, ZPE $\text{OH}_2 = 21.08$ kJ/mol, which differ by 5, 3% and fluctuate [8].

Moreover, electron density of the two small systems, that of hydrocarbon (several CH groups) and that of water molecules forced by hydrocarbon from the cavity, is approximately the same.

Having dealt with the duality of measurement units $\Delta H_{T=0}$, we shall write a new equation (3) now taking into account quantum and thermal fluctuations so that this duality becomes visible

$$\Delta H_i = T_c \Delta S_i + 1/2 \hbar \omega, \quad (4)$$

where $1/2 \hbar \omega$ is the energy of the quantum harmonic oscillator or ZPE, $\hbar$ is the reduced Planck constant, ω is the angular frequency of the harmonic oscillator or the frequency of the O-H bond stretching mode. Equation (3) already refers to quantum or stochastic thermodynamics that has just begun to develop [9].

For the phase transition in the water + hydrocarbon system we have $\Delta H_i = 4.9$ kJ / mol, $T_c = 298\text{K}$, then $\Delta S_i = 16.44$ J / molK. For a phase transition in water at 273K $\Delta S_i = 17.94$ J/molK. Due to quantum fluctuations the change in entropy decreased by 1.5 J / molK, i.e. by 8.36%. This corresponds to $\Delta H_i = 0.447$ kJ / mol or 1.9% of the total possible quantum contribution of 22.48 kJ/mol. It can be assumed that quantum fluctuations make very little or no contribution to the hydrophobic hydration of hydrocarbons, because there is no merging of their molecules in the process.

In the process of micelle formation for a series of 35 non-ionic surfactants, according to the experimental data of the compensation effect at 298K, we obtained $T_c = 222\text{K}$

$$\Delta H_i = 222 \cdot \Delta S_i - 18,09. \quad (5)$$

T_c coincides with the temperature of the hypothetical second critical point of water at 223K and may serve as a confirmation of its existence, which is being discussed now. It is believed that at 223K, an equilibrium of ultraviscous fluctuations of light and heavy water is observed in water, or the equilibrium of enthalpy and entropic thermal fluctuations, according to our hypothesis,. Therefore, we can assume that the liquid-liquid phase transition during micelle formation of non-ionic surfactants is similar to the phase transition in supercooled water near the second critical point, and micelle formation resembles spontaneous emulsification. This is also confirmed by the fact that to search for this specific

point of water researchers used reverse microemulsions of water in the hydrocarbon with a non-ionic surfactant sorbitan tristearate [10].

In the process of micelle formation for a series of 23 ionic surfactants, according to the experimental data of the compensation effect at 298 K, we obtained $T_c=319\text{K}$

$$\Delta H_i = 319 \cdot \Delta S_i - 22,41. \quad (6)$$

Spontaneous processes with ionic surfactants gain in ZPE by 4.39 kJ/mol more in comparison with non-ionic surfactants. T_c coincides with the temperature of the minimum isothermal compressibility of water. It can be shown [5] that the change in the Gibbs energy of the formation of a cavity in water with temperature is

$$\Delta G_{cav.} = \frac{V_{cav.}}{\chi_T}, \quad (7)$$

where $V_{cav.}$ is the volume of the cavity for accommodating surfactant molecules, χ_T is the isothermal compressibility of water. Therefore, we can say that water in the process of the liquid-liquid phase transition at 298K behaves in such a way that the systems described by equation (4) get a maximal gain in the Gibbs energy of the formation of a cavity for the placement of micelles and surfactant molecules in the same way as water at 319K.

In the process of dissolution of hydrocarbons systems lose in Gibbs energy. They have to spend energy building a special structure of water around hydrocarbon molecules. Therefore, the sign of $\Delta H_{T=0}$ in Eq. (3) is positive. In the case of a spontaneous micelle formation, the system gains in Gibbs energy due to the SCES. Therefore, the sign of $\Delta H_{T=0}$ is negative.

$\Delta H_{T=0}$ is directly proportional to the length of the surfactant chain [11]. Therefore, it is possible to calculate the contribution of ZPE_{CH_2} to the Gibbs energy of micelle formation corresponding to the methylene group of ionic and non-ionic surfactants. This value does not depend on the standard states of the thermodynamic process, methods for calculating the enthalpy and entropy of micelle formation, and therefore it more accurately characterizes the role of water ZPE in micelle formation than $\Delta H_{T=0}$. ZPE_{CH_2} for ionic surfactants is -3.9 kJ/mol and is similar to $G_{CH_2}^0 = -3.7$ kJ/mol under standard conditions, and for not ionic surfactants, it is equal to -2.9 kJ/mol [12].

This value of $ZPE_{CH_2} = G_{CH_2}^0 = -2,9$ kJ/mol shows the maximum gain in energy that can be obtained through using the participation of thermal fluctuations in the process under standard conditions. Despite this equality, we cannot conclude that cavities in water for micelles of non-ionic surfactants are formed only due to ZPE. Due to the lack of a concept that combines quantum thermodynamics with conventional thermodynamics (quantum and thermal fluctuations) it is necessary to take into account other parameters and rationales that we provide here.

For ionic surfactants, the contribution of ZPE_{CH_2} is 34% greater than that of nonionic surfactants, despite the charged micelle surface. Then the fraction of ZPE, that is unknown to us so far, under standard conditions should be equal to ~ 1.3

kJ/mol. Indeed, the long-term contribution $G_{CH_2}^0 = 1.4$ kJ/mol under standard conditions [5] is a “fingerprint” or veiled contribution of ZPE_{CH_2} . The change in the Gibbs energy during the micelle formation of ionic surfactants is written as

$$\Delta G_{mic.}^0 = RTCMC + \beta CMC, \quad (8)$$

where β is the degree of condensation of ions on micelles. Thus, β or the degree of dissociation of micelles $\alpha = 1 - \beta$ indicate the contribution of ZPE_{CH_2} to micelle formation. For comparison, for non-ionic surfactants [11]

$$\Delta G_{mic.}^0 = RTCMC \quad (9)$$

Quantum fluctuations make micelles 34% stronger than micelles of non-ionic surfactants at 298 K and atmospheric pressure. The water cavity for the placement of micelles is strengthened by SCES.

2. Cooperative effect

In the processes of solubilization, hydrotropy, and condensation of two organic ions with opposite charges we found a cooperative effect [5]. At the same temperature and pressure, a directly proportional relationship was found between the Gibbs energy of aggregation and the total volume (length of the hydrocarbon radical) of the intermolecular interaction partners. The cooperative effect can be used to test the existence of SCES. For this it is necessary to find the contribution of the Gibbs energy of the process into the methylene group. For the hydrotropy process, it does not depend on the choice of systems. We will get the same Gibbs energy contribution regardless of the length of the hydrocarbon radical of the salting-in agent and the salted-in substance. For the solubilization process we get a different result.

If we investigate the solubilization of the homologous series of ethane, propane, and butane in solutions of sodium dodecyl sulfate, then $\Delta G_{mic.}^0 = -3.7$ kJ/mol. If we investigate the solubilization of propane in micellar solutions of the homologous series of sodium alkyl sulfates C8, C10, C12, we get $\Delta G_{mic.}^0 = -1.4$ kJ/mol [5]. Such hysteresis or duality of properties is due to SCES or, in other words, due to the presence of various contributions of thermal and quantum fluctuations of water to the hydrophobic interaction of ionic surfactants. In the first group the solubilization studies yield information on the overall contribution of thermal and quantum fluctuations to solubilization. In the second group of studies, information is obtained only about quantum fluctuations. When methylene groups are added to the systems by solubilization, SCES decoherence does not occur. As you can see, the result depends on the method of "spying" on the SCES. Solubilized methylene groups of hydrocarbons in the cooperative system do not differ from others present in dissolved surfactants.

If we investigate SCES by conductometry and potentiometry, then the device affects the systems and a decoherence of SCES occurs. The parameter α is obtained, but this parameter changes significantly, it is not measured precisely, which confirms the existence of nonlocality (CECS) in the system.

3. Small and wide angle X-ray scattering

X-ray scattering characterizes the time-averaged structural organization of water molecules, surfactants, and micelles. X-rays are scattered by the electron density of water and surfactant molecules, and the scattering cross section or intensity $I(Q)$ increases in direct proportion to the number of electrons (electron density) or the atomic number of an element. X-ray diffractometer SAXSessmc2 (Anton Paar GmbH, Austria) allows measurements in the range of values of the modulus of the wave vector Q of X-ray scattering from 0.03 to 28 nm⁻¹. Q is defined as $Q = (4\pi/\lambda) \sin(\Theta/2)$, where λ is the wavelength of the incident X-ray radiation, and Θ is the scattering angle. Using the spectrum of small-angle X-ray scattering (SAXS) in the range of about $Q = 0.6$ -2 nm⁻¹, we can obtain information on the diameters of surfactant micelles (cavities for micelles). Beginning at $Q > 10$ nm⁻¹, wide angle X-ray scattering (WAXS) takes place. The Q error of the system is 0.03 nm⁻¹.

Using SAXSessmc2 about $Q = 1.5$ nm⁻¹ we tested [5, 13] thermal fluctuations (cavities) in water for placing SDS micelles that had a diameter of ~ 6 nm. In addition, the O... O correlations were investigated in the first coordination sphere of water ~ 0.33 nm near $Q = 19.8$ nm⁻¹, where one could expect the appearance of quantum fluctuations.

With an increase in the concentration of SDS up to CMC, the intensity $I(Q)$ in the first coordination sphere of water increased from 8250 photon pulses for water to 8750 photon pulses for SDS solutions 0.01 mol / L, and then decreased. This result shows that the electron density at a water size of ~ 0.33 nm in SDS solutions up to CMC = 0.01 mol/L first increases and then decreases as a result of a decrease in the water content in the solution. The increase can be even greater if we take into account the decrease in the amount of water in the solution to 0.01 mol/L. By increasing the electron density of water, you can calculate an approximate decrease in the volume of water by $8750 - 8250 / 8250 \times 100 = 6\%$. To compress the volume of water by 6%, it is necessary to apply a pressure of 13200 atm. With an increase in pressure only in water, the O... O correlation decreases, and the frequency of the O – H stretching mode increases [14], which is consistent with an increase in the energy of quantum fluctuations $\hbar\omega$.

With equal concentrations 0.1 M of SDS, depending on temperature the values $Q_{\max}$ and $I(Q_{\max})$ of the first peak of water fluctuate abnormally (Table 1).

Table 1. The scattering maximums $Q_{\max}$ and intensities $I(Q)$ of X-ray scattering in the region of the first peak of water in aqueous solutions of SDS with the concentration of 0.1 mol/L at different temperatures.

t [°C]	$Q_{\max}$ [nm ⁻¹]	$I(Q)_{\max}$ [pulses]
3,9	18,20	7773
5	18,83	8306
10	18,68	7737
15	18,71	8168

30	19,49	7648
40	19,45	7429
50	19,63	7415
60	20,02	7889
70	19,40	7601

Both data sets for water [15] show that the position of $Q_{\max}$ increases proportionally to temperature, and the amplitude of $I(Q)$ decreases proportionally to temperature, which is consistent with the structural properties of water.

Thus, to create water cavities of micelles of ionic surfactants with a size of 4-6 nm (thermal fluctuations), water is compressed to a size of 0.1-0.3 nm (quantum fluctuations) throughout the total water volume. Quantum fluctuations are nonlocal.

4. Dynamic light scattering

The research by means of dynamic light scattering (DLS) with a Zetasizer Nano ZS analyzer (Malvern Instruments Ltd, UK) allows us to investigate the dynamics of inhomogeneities in water [13]. In routine experiments the hydrodynamic radii of solid nanoparticles are determined easily. For micellar solutions, the device developers recommend determining the size of micelles in the presence of large amounts of inorganic salt, when, as it will be shown below, the disappearance of SCES occurs. When scattering in micellar solutions the incident monochromatic wave is split into several waves with changed frequencies $\omega + \Delta\omega$ and $\omega - \Delta\omega$. Each splitting $\Delta\omega$ corresponds to its own fluctuation. Based on the scattering of light by fluctuations, the theory of DLS was proposed in terms of the autocorrelation function. The scattering analysis includes, first, the determination of the constant Γ of the decreasing autocorrelation function that is proportional to the width of the scattering spectrum and is related to the diffusion coefficient of inhomogeneities. The diffusion coefficient of inhomogeneities D , in its turn, is related to their hydrodynamic diameter, which is shown by the device.

Testing the dynamics of inhomogeneities in a 0.01M SDS solution showed the existence of three fluctuations with diameters of 1.28, 185, 603 nm with their content of 23, 61 and 16% respectively. With the addition of 0.01M NaCl, the size of fluctuations changed to 3.56, 209 and 5019 nm with their content of 74, 23 and 3%. Since we are interested in space-time fluctuations, we can conclude that the diffusion coefficients D of micelles (cavities) are the smallest and differ from each other insignificantly. The diffusion coefficients of the other two, apparently quantum fluctuations are not predictable. They change. With the addition of salt, the sizes of micelles are manifested more clearly, while quantum fluctuations gradually disappear with increasing NaCl concentration. As shown below, quantum fluctuations appear as chains of achiral spirals of water molecules. The DLS method characterizes them as a sphere with a diameter equal to the length of the achiral water chain. That is why the spheres are so large compared to micelles.

5. Visible circular dichroism

The spectra of visible circular dichroism are obtained by spectrum polarimeters in the coordinates: the difference in absorption intensity (ellipticity) depending on the wavelength of electromagnetic radiation [16]. Ellipticity ε is measured in units of $\text{deg} \cdot \text{cm}^2 \cdot \text{dec} \cdot \text{mol}^{-1}$ (Fig. 1). When linearly polarized light passes through a circular dichroic sample, it becomes elliptically polarized. Molecules of conventional surfactants, such as SDS, do not have asymmetric carbon atoms. Lutein (β , ε -carotene-3, 3'-diol) is chiral.

We used it in 1000 times lower concentrations than SDS in the form of a label to study the chiral properties of quantum fluctuations of water in the micelle formation region (Fig. 1). The circular dichroism spectra of lutein had positive and negative extrema before and after the crossover at 390 nm before the CMC of DDS in the region 0.002-0.004 M. With an increase in the concentration of DDS in the region 0.008-0.015 M (after CMC), the sign of the extrema changed to the opposite.

As a result of the SCES of water and the aggregation of SDS, an inversion in chirality occurs. Positive 1 and 2, and negative 3 and 4 circular dichroism stripes (Fig. 1), that are caused by the formation of helical exciton doublets (multiplets) of lutein, might coexist with helical exciton multiplets of water. At 0.004-0.008 M (CMC), a chirality inversion is observed due to the prevalence of opposite exciton multiplets in the solution. Spiral exciton doublets of water can consist of achiral spirals of water molecules united by proton tunneling.

Fig.1. The spectrum of visible circular dichroism of lutein in an aqueous solution (4.6 μmol) depending on the concentration of SDS at 25 °C: 1 - 0.002, 2 - 0.004, 3 - 0.008, 4 - 0.015 M; 1 and 2 positive, 3 and 4 negative bands of circular dichroism before and after the crossover point 390 nm. The bands are a consequence of the formation of spiral

doublets of lutein together with spiral doublets of water. At 0.004-0.008 M (CMC), inversion of chirality is observed.

A similar phenomenon was observed with an increase in the optical rotation of solutions before the CMC of SDS from 0.002 mol/L, and its decrease after CMC down to a constant value at 0.015 mol/L [17].

Laser-induced temporal changes in light scattering Hv, Vv and Dv at 90 ° were measured in aqueous solutions of ionic surfactants both above and below the CMC. The intensities Hv and Vv decreased exponentially from the moment of the first illumination with a time constant of the order of ~2 s for an incident power density of $\geq 50 \text{ W / cm}^2$ from an argon ion laser. Authors [18] explained the phenomenon by the existence of a strong anisotropic structure around the CMC of ionic surfactants. This phenomenon was absent in the solutions of non-ionic surfactants.

Findings

Equations of the compensation effect for the processes of dissolution of hydrocarbons and micelle formation of surfactants make it possible to determine the temperatures of specific points of water: melting / crystallization temperature, the minimum of isothermal compressibility, and the second critical point in the supercooled state. By using the cooperative effect, it is possible to determine the total energy of thermal and quantum fluctuations in hypothetical liquid water at $T = 0\text{K}$ and compare it with the Gibbs energies under standard conditions. The obtaining of accurate values of changes in the Gibbs energies of micelle formation processes under standard conditions is complicated by the standardization of the beginning of the process in aqueous solutions. Changes in the thermodynamic functions of the micelle formation process are calculated relative to 1 molar fraction of surfactant in a "hypothetical diluted solution", which does not agree with reality. Similar problems arise in the interpretation of thermal effects. This is customary in the thermodynamics of solutions. Therefore, it is better to compare thermodynamic functions corresponding to the volume of water per methylene group, which does not depend on standard conditions.

For ionic surfactants, the contribution of ZPE_{CH_2} is larger than that of non-ionic surfactants by ~ 1.3 kJ/mol. It is approximately equal to the contribution of $G_{CH_2}^0 = 1.4 \text{ kJ/mol}$ under standard conditions and is a "fingerprint" or veiled contribution of ZPE_{CH_2} . The contribution to the Gibbs energy of micelle formation, which is allegedly associated with the dissociation of micelles, determines the magnitude of nonlocality or SCES, as shown here. Quantum fluctuations of water make micelles of ionic surfactants more durable than micelles of non-ionic surfactants at 298 K and atmospheric pressure. The water cavity for the placement of micelles is strengthened by SCES.

Experimental studies of the solubilization of n-hydrocarbons in micellar solutions of alkyl sulfates and the processing of these data by the cooperative effect

confirmed approximate equality of water ZPE_{CH_2} and $G_{CH_2}^0$ obtained by the compensation effect.

By means of SAXS and WAXS it was possible to show that for the appearance of micelle cavities with a size of 4-6 nm (thermal fluctuations), water molecules have to contract throughout the volume at a size of 0.1-0.3 nm due to quantum fluctuations. Thanks to these methods fluctuations can be characterized as the time-averaged structural organization of water molecules in space.

The dynamic organization (space-time) of water and micelles was investigated by dynamic light scattering. The method made it possible to trace different types of fluctuations by diffusion in the same units of its measurement. Although thermal and quantum fluctuations live in the femtosecond range, the method allows them to be distinguished and draw conclusions about their dynamic organization. The diffusion coefficients of micelles (cavities) are the smallest and differ from each other insignificantly depending on the surfactant (water) concentration. The diffusion coefficients of the other two, apparently quantum fluctuations, are much larger and differ from each other. They vary with the concentration of water and the addition of inorganic salt. With the addition of salt, the sizes of micelles appear more clearly, and quantum fluctuations gradually disappear with increasing NaCl concentration. With the addition of salt a gradual decoherence of SCES occurs.

As shown by chiral spectroscopy, quantum fluctuations of water near the CMC of a surfactant have anisotropic properties. We can assume the existence of rings and spirals of water molecules, rotating in different directions with different speeds when passing through the region of the CMC surfactant.

When discussing SCES as a correlation of thermal and quantum fluctuations, we mean the correlation of the electron density of one type with the electron density of another. Fluctuations are called differently, because they are described in different theories of thermodynamics and quantum mechanics. Quantum thermodynamics combines these two theories. It may offer a combined name of these fluctuations.

Methods

We have interpreted the nature of the quantities in the equations of the compensation effect for the first time. In order to calculate equation (3) we used the data from [19].

Equations (5) and (6) are taken from [20]. It also presents standard errors of $\Delta H_{T=0}$, T_c and surfactants, solutions and parameters of which were used for the calculation. Operations with the compensation equations of ionic surfactants show that the more compensation measurements are made, the smaller the error is and the parameters of the equations become more accurate. This is similar to tossing a coin for heads or tails. Only with a large number of trials you can get heads or tails fifty-fifty.

To measure the spectrum of visible chiral dichroism, a suitable concentrated solution of lutein in ethyl alcohol is prepared. A few drops of this solution are

added to an aqueous solution of SDS before and after CMC to a SDS / lutein ratio of 1000/1 with stirring. The spectrum is measured by a JASCO J500 spectropolarimeter (Fig. 1).

Acknowledgements

This research was supported by the Ministry of Education and Science of the Russian Federation, state assignment No. 0851-2020-0035. Prof. Mirgorod thank Anastasia Storozhenko and Alexander Chekadanov for fruitful discussions.

Competing interests

The author declare no competing interests.

References

1. Tokura, Y.; Kawasaki, M.; Nagaosa, N. Emergent functions of quantum materials. *Nature Physics* **13**, 1056-1068 (2017).
2. Sanket, A. D. et. al. Water ordering controls the dynamic equilibrium of micelle–fibre formation in self-assembly of peptide amphiphiles. *Nat. Commun.* **24**, 12367-12377 (2016).
3. Tanbour, R. et. al. Drug Delivery Systems Based on Polymeric Micelles and Ultrasound. A Review. *Current Pharmaceutical Design* **22**, 1-12 (2016).
4. Anic, D. J. Zero Point Energy of Polyhedral Water Clusters. *J. Phys. Chem. A* **109**, 5596-5601 (2005).
5. Mirgorod, Yu.A.; Dolenko, T.A. Liquid Polyamorphous Transition and Self-Organization in Aqueous Solutions of Ionic Surfactants. *Langmuir* **31**, 8535-8547 (2015).
6. Liu, L.; Guo, Q.-X. Isokinetic Relationship, Isoequilibrium Relationship, and Enthalpy–Entropy Compensation. *Chem. Rev.* **101**, 673-695 (2001).
7. Ceriotti, W. et. al. Nuclear Quantum Effects in Water and Aqueous Systems: Experiment, Theory, and Current Challenges. *Chem. Rev.* **116**, 7529-7550 (2016).
8. Irikura, K. K. Experimental Vibrational Zero-Point Energies: Diatomic Molecules. *J. Phys. Chem. Ref. Data* **36**, 389-397 (2007).
9. Deffner, S. and Campbell, S. *Quantum Thermodynamics: An introduction to the thermodynamics of quantum information* (Morgan & Claypool Publishers, 2019).
10. Mishima, O.; Stanley, H. E. Decompression-Induced Melting of Ice IV and the Liquid–Liquid Transition in Water. *Nature* **392**, 164–168 (1998).
11. Chen, L.J.; Lin, S.Y.; Huang, C.C. Effect of Hydrophobic Chain Length of Surfactants on Enthalpy–Entropy Compensation of Micellization. *J. Phys. Chem. B* **102**, 4350–4356 (1998).
12. Nichikido, N.; Matuura, R. The Effect of Added Inorganic Salts on the Micelle Formation of Nonionic Surfactants in Aqueous Solution. *Bull. Chem. Soc. Japan* **50**, 1690-1694 (1977).

13. Mirgorod, Yu.; Chekadanov, A.; Dolenko, T. Structure of Micelles of Sodium Dodecyl Sulphate in Water: an X-ray and Dynamic Light Scattering Study. *Chem. J. Moldova* **14**, 107-119 (2019).
14. Romanenko, A. V. et. al. In Situ Raman Study of Liquid Water at High Pressure. *Applied Spectroscopy*, **10** (2018).
15. Hughes, S.W.; Barry, J. The first x-ray diffraction peak of water as a function of temperature in the range 4–63 °C. Preprint at https://eprints.qut.edu.au/68433/1/AS_13_poster.pdf
16. *Chiral Analysis: Advances in Spectroscopy, Chromatography and Emerging Methods*. Edited P.L. Polavarapu (Elsevier, 2018).
17. Rusanov, A. I.; Nekrasov, A. G. One More Extreme Near the Critical Micelle Concentration: Optical activity. *Langmuir* **26**, 13767 -13769 (2010).
18. Farinato, R.S.; Rowell, R.L. Transient Light Scattering in Aqueous Surfactant Systems. *J. Colloid and Interface Science* **66**, 483-489 (1978).
19. Belousov, V.P.; Panov V.Yu. *Thermodynamic properties of aqueous solutions of organic substances* (CRC Press, 1994).
20. Golicoeur, C.; Philip, P.R. Enthalpy-Entropy Compensation for Micellization and their Hydrophobic Interactions in Aqueous Solutions. *Canadian J. Chem.* **52**, 1834 – 1839 (1974).