

DOI: 10.17516/1997-1397-2022-15-6-763-775

УДК 535.375.55

The Influence of Amphiphilic Compounds Self-organization on the Fermi Resonance Contribution in the OH-groups Stretching Band Formation

Ivan V. Plastinin*

Tatiana A. Dolenko†

Sergey A. Burikov‡

Skobeltsyn Institute of Nuclear Physics

Lomonosov Moscow State University

Faculty of Physics, Lomonosov Moscow State University

Moscow, Russian Federation

Sergey A. Dolenko§

Skobeltsyn Institute of Nuclear Physics

Lomonosov Moscow State University

Moscow, Russian Federation

Received 10.07.2022, received in revised form 15.09.2022, accepted 20.10.2022

Abstract. The role of Fermi resonance (FR) in the formation of the OH-groups Raman spectra stretching band of aqueous solutions of amphiphilic compounds with different lengths of hydrocarbon radicals: ethanol and sodium octanoate, has been studied. The influence of amphiphile self-organization processes on the FR contribution to the intensity of the OH stretching band of aqueous solutions was found.

Keywords: amphiphiles, self-organization, Fermi resonance, aqueous solutions, Raman spectroscopy, genetic algorithms.

Citation: I.V. Plastinin, T.A. Dolenko, S.A. Burikov, S.A. Dolenko, The Influence of Amphiphilic Compounds Self-organization on the Fermi Resonance Contribution in the OH-groups Stretching Band Formation, *J. Sib. Fed. Univ. Math. Phys.*, 2022, 15(6), 763–775.

DOI: 10.17516/1997-1397-2022-15-6-763-775.

Introduction

The ability of amphiphilic compounds to self-organize is actively used in various industries, nanotechnologies, and pharmaceuticals [1–4]. In all applications, it is necessary to carry out diagnostics of the processes occurring in the environments. Raman spectroscopy is one of the most promising methods for non-contact and express diagnostics of technological environments with amphiphilic substances. It was shown in [5–8] that the processes of surfactants self-organization manifest in Raman spectra of their aqueous solutions: the formation of spherical micelles, the

*plastinin_ivan@mail.ru <https://orcid.org/0000-0003-2059-0960>

†tdolenko@mail.ru <https://orcid.org/0000-0003-2884-8241>

‡sergey.burikov@gmail.com <https://orcid.org/0000-0003-2271-8980>

§dolenko@srd.sinp.msu.ru <https://orcid.org/0000-0001-6214-3195>

© Siberian Federal University. All rights reserved

transformation of spherical micelles to nonspherical ones, changes in the conformation of hydrocarbon radicals, etc. This allows using laser Raman spectroscopy not only to identify these processes, but also to determine with good accuracy the values of critical micelle concentrations (CMC), in particular, CMC_1 , at which spherical micelles are formed from surfactant monomers [9, 10].

However, for a more effective application of Raman spectroscopy in the diagnostics of surfactant solutions, it is necessary to understand the nature of the spectra. At present, the mechanisms of formation of the Raman spectral bands of water in aqueous solutions of self-organizing amphiphilic compounds have not been adequately studied. In particular, the contribution of the FR — resonance between the symmetric stretching vibration of the water OH groups (ν_1) and the overtone of the bending vibration of H–O–H ($2\nu_2$) — to the OH groups stretching band is not clear [11, 12]. It is assumed that the width of the OH groups stretching band is due to the intense component of the Fermi doublet in the low-frequency region of the band [11–13]. According to the data of the authors of [14], it is the contribution of the FR to the intensity of the OH stretching band that determines its singularity in the region of 3250 cm^{-1} .

In this study, we investigated the contribution of FR ($\nu_1, 2\nu_2$) to the intensity of the OH groups stretching band during self-organization of amphiphilic compounds in aqueous solutions. Ethanol and sodium octanoate were used as amphiphilic compounds. These substances have different lengths of hydrocarbon radicals, which directly affects the features of self-organization of these amphiphilic substances. Sodium octanoate is a surfactant that forms micelles at concentrations of about 0.4 M in water [9]. Ethanol cannot form micelles, but at certain concentrations it forms associates of water and alcohol molecules [15], and, like many alcohols, it can act as a cosurfactant, facilitating the formation of micelles [10]. The Raman spectra of aqueous solutions of ethanol and sodium octanoate were obtained. To extract information about the contribution of the FR to the OH groups stretching band, a modern optimization method — genetic algorithms — was applied.

1. Materials and methods

1.1. Materials

To prepare the aqueous solutions of amphiphilic compounds, we used ultrapure deionized bidistilled water (H_2O) obtained in a Millipore Simplicity UV water filtration and purification system. Water resistance was $18.2\text{ M}\Omega\cdot\text{cm}$ at $25\text{ }^\circ\text{C}$.

The following amphiphilic compounds were used:

- ethanol (C_2H_5OH , CAS:64-17-5, OJSC Medkhimprom (Russia), 95 wt. %),
- sodium octanoate ($C_8H_{15}NaO_2$, CAS:1984-06-1, Sigma-Aldrich (Germany), 99.8 wt. %).

Water-ethanol solutions with concentrations from 0 to 96 vol.% and aqueous solutions of sodium octanoate (NaC_8) with concentrations from 0 to 2.1 M were prepared. All aqueous solutions of surfactants were at temperatures above the Krafft point T_{Kr} (for NaC_8 , $T_{Kr} < 0\text{ }^\circ\text{C}$ [16,17]).

1.2. Methods

Raman spectroscopy

The Raman signal was excited by radiation from an LG106M4 argon ion laser (wavelength — 488 nm; power — 500 mW). To suppress scattering at the unshifted frequency, a 488 nm long-

wavelength edge filter RazorEdge LP02-488RE-25 was used, which makes it possible to approach the laser excitation line up to 100 cm^{-1} . The spectra were recorded in 90° experimental geometry. A film polarizer (contrast not worse than 1:70) was used to record polarized and depolarized spectra. The spectrum registration system included a monochromator (Acton 2500i, gratings 1800 and 900 grooves/mm, focal length 500 mm) and a CCD camera (Syncerity, Jobin Yvon). The recording time for one spectrum was 2 min. The spectral resolution in the region of the stretching band of water is 1.5 cm^{-1} . The processing of the spectra consisted in correcting for the laser power and the spectral sensitivity of the registration system, subtracting the pedestal. The temperature of the samples was controlled by a KRIO-VT-01 thermal stabilization system and maintained constant at $25.0 \pm 0.1^\circ\text{C}$.

Genetic algorithms

To decompose the spectrum bands into components by the method of genetic algorithms (GA), the add-in "Solver" developed by Frontline Systems for Microsoft Excel was used. GA ensured finding the neighborhood of the minimum of the residual functional. Further use of the method of generalized reduced gradient descent (Generalized Reduced Gradient, GRG2, "Solver", Excel) made it possible to determine the minimum of the residual functional more accurately. It should be noted that the use of such powerful optimization methods does not require the presence of an a priori model of oscillatory processes, which reduces the ambiguity of the solution of this ill-posed inverse problem.

2. Results and discussion

2.1. Fermi resonance during self-organization of non-micelle-forming compounds in water

Integral (non-polarized) Raman spectra of water-ethanol solutions with ethanol content from 0 to 96 vol. % were obtained (Fig. 1a). With an increase in the concentration of alcohol, not only the ratio of the intensities of the stretching bands of the ethanol CH groups ($2800\text{--}3000\text{ cm}^{-1}$) and the OH groups of water and alcohol ($3000\text{--}3800\text{ cm}^{-1}$) changes, but the shape of the OH groups stretching band (Fig. 1a). To quantify this change, the ratio of the intensity of the OH stretching band in the region of lower wavenumbers (3200 cm^{-1}) to the intensity of the OH band in the region of large wavenumbers (3420 cm^{-1}) was used (Fig. 1a). This ratio characterizes the proportion of the number of strong and weak hydrogen bonds in solution. It was found that the ratio I_{3200}/I_{3420} behaves non-linearly with an increase in the concentration of ethanol in water: a maximum is observed in the concentration range of 20 vol. %, and a sharp decrease is observed at concentrations greater than 20 vol. % (Fig. 1b).

This behavior of the intensity ratio I_{3200}/I_{3420} dependence on the alcohol concentration is explained by the change in the energy of the hydrogen bond between the molecules in the water-alcohol solution at different ratios of the solution components. At an alcohol concentration of 20 vol. %, as a result of self-organization processes, the solution structure is stabilized by ethanol molecules and hydrogen bonds between the hydroxyl groups of water and ethanol are strengthened, which is consistent with the data of many authors [18–23].

To estimate the contribution of the Fermi resonance (FR), water-ethanol solutions with different strengths of hydrogen bonds were chosen: water, water-ethanol solutions with ethanol concentration 20 % and 70 %.

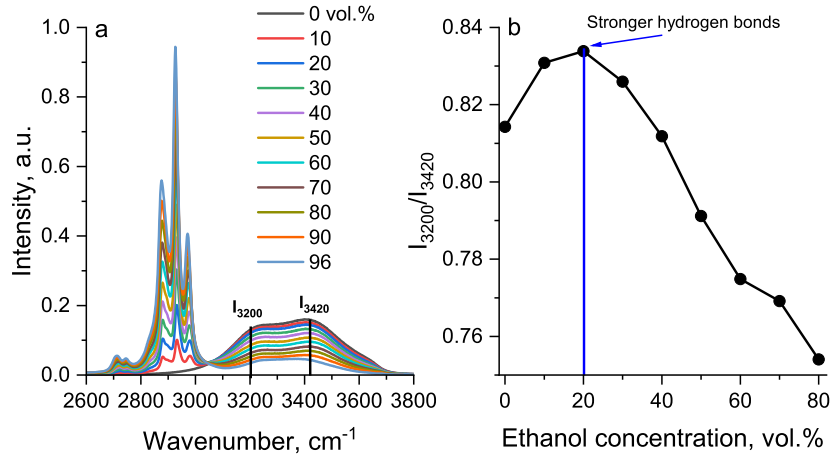


Fig. 1. Integral spectra of water-ethanol solutions with different alcohol content (a); dependence of the ratio of intensities at the wavenumbers 3200 cm⁻¹ and 3420 cm⁻¹ of the OH groups stretching band of water-ethanol solutions on the concentration of ethanol (b)

Since the participants of FR are only the vibrations of the same symmetry, the polarized (I_{pol}) and depolarized (I_{dep}) Raman spectra of solutions in the region of 2700–3700 cm⁻¹ were recorded in experiment. Then, isotropic and anisotropic spectra were calculated, in which symmetric and asymmetric vibrations are separated (Fig. 2) [24]:

$$I_{iso} = I_{pol} - 4/3I_{dep}; \quad I_{aniso} = 4/3I_{dep}. \quad (1)$$

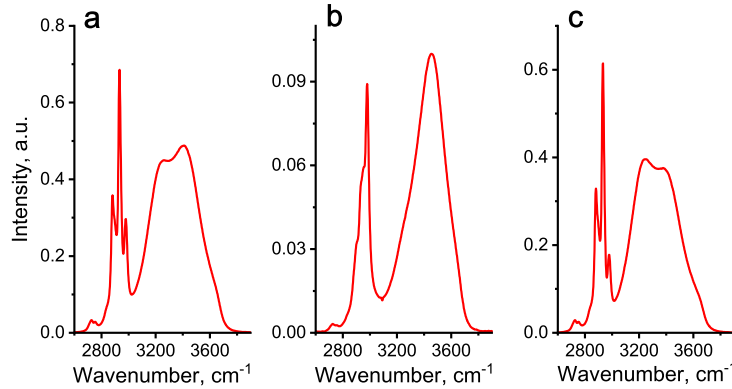


Fig. 2. Bands of stretching vibrations of CH- and OH-groups of the polarized (a), depolarized (b) and isotropic (c) Raman spectra of a 20% ethanol solution in water

Estimation of the FR contribution to the OH groups stretching band intensity in water and in aqueous ethanol solutions

The contribution of the Fermi resonance to the spectral band intensity is determined by the interaction constant W [12, 25, 26]. As follows from the theoretical concepts of FR [25], to determine the FR interaction constant $W = \frac{\sqrt{\Delta^2 - \Delta_0^2}}{2}$, it is necessary to find the values of

wavenumber intervals Δ_0 and Δ between unperturbed and perturbed vibrational levels, respectively. The wavenumber interval Δ_0 between unperturbed vibrational levels of OH groups was determined earlier in [26] and equals $\Delta_0 = 150 \pm 7 \text{ cm}^{-1}$.

The wavenumber intervals Δ between the vibrational levels of the OH groups perturbed by the Fermi resonance was determined from the experimentally obtained isotropic OH groups stretching bands of water-ethanol solutions (Fig. 2c). Based on model concepts about the structure of the OH groups stretching band [26–29], we decomposed the isotropic stretching bands of all samples into four Gaussian components using genetic algorithms.

It was found that the OH groups stretching bands of all the studied samples are described with good accuracy by four components of the Gaussian form (Fig. 3). Based on the existing model concepts of the water structure [26–29], it can be assumed that the isotropic stretching band consists of an overtone of bending vibrations with C_{2v} symmetry (component 1), symmetric stretching vibrations with C_{2v} symmetry (component 3), and symmetric stretching vibrations of molecules with other symmetry C_s , not participating in the FR (component 2). In addition, the spectrum contains vibrations of weakly bound water molecules with C_{2v} symmetry (component 4), which manifest themselves in the region of 3630 cm^{-1} . They do not participate in resonance, since their frequencies are too far from the bending vibrations overtone frequency.

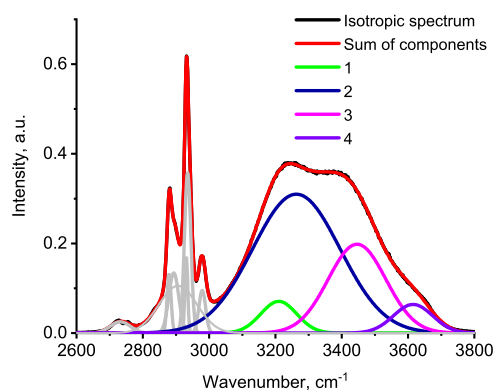


Fig. 3. Decomposition of the OH groups stretching vibrations band of an aqueous ethanol solution (20 vol. % ethanol) into Gaussian contours (decomposition components of the band of CH groups stretching vibrations of ethanol are highlighted in gray)

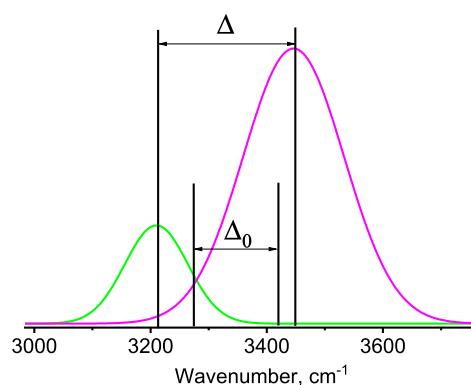


Fig. 4. Determination of wavenumber interval Δ between perturbed vibrational levels of OH groups in a 20% ethanol solution at $25 \text{ }^\circ\text{C}$

Thus, from physical considerations, two components of the OH groups isotropic stretching band, components 1 and 3, can be interpreted as a Fermi doublet (with frequencies of maxima $2\nu_2$ and ν_1 , respectively). The OH stretching bands were decomposed several times to determine the mean values of $2\nu_2$ and ν_1 and their standard deviations. Then the wavenumber intervals Δ was found between the perturbed vibrational levels for each of the samples (Fig.4). The obtained values Δ are presented in Table 1.

Taking into account the obtained wavenumber intervals Δ_0 and Δ , the FR interaction constant W was calculated using the formula $W = \frac{\sqrt{\Delta^2 - \Delta_0^2}}{2}$

Thus, for water at room temperature: $\Delta = 3410 - 3210 = 200 \text{ cm}^{-1}$. Using the obtained wavenumber intervals $\Delta_0 = 150 \text{ cm}^{-1}$ and $\Delta = 200 \text{ cm}^{-1}$, we calculated the interaction constant of the Fermi resonance in water at a temperature of 25 °C:

$$W = \frac{\sqrt{\Delta^2 - \Delta_0^2}}{2} = 66 \text{ cm}^{-1}$$

At the same temperature, the contribution of the FR to the intensity of the water stretching band (in percent) was estimated using the following formula [11]:

$$I_{2\nu_2}/(I_{2\nu_2} + I_{\nu_1}) * 100 \% = (\Delta - \Delta_0)/2\Delta * 100 \% \approx 13 \%$$

This means that the contribution of the Fermi doublet component corresponding to the bending vibrations overtone to the intensity of the water stretching band is 13% of the total intensity of the Fermi doublet at a temperature of 25 °C. The calculation results are presented in Tab. 1.

Table 1. Calculated interaction constants W and FR contributions to the intensity of the OH group stretching band for water and aqueous ethanol solutions at a temperature of 25 °C

| Solution | $\Delta_0, \text{ cm}^{-1}$ | $\Delta, \text{ cm}^{-1}$ | $W, \text{ cm}^{-1}$ | Contribution, % |
|--------------|-----------------------------|---------------------------|----------------------|-----------------|
| Water | 150±7 [26] | 200±1 | 66±4 | 13±2 |
| 20 % ethanol | 150±7 [26] | 238±1 | 93±5 | 19±1 |
| 70 % ethanol | 150±7 [26] | 193±1 | 61±4 | 11±2 |

In a 20 % solution, as a result of self-organization of ethanol molecules, associates of water and alcohol with strong hydrogen bonds are formed (Fig. 1b), in which the frequency of symmetric stretching vibrations ν_1 "shifts" to the low-frequency region and "approaches" the overtone frequency of bending vibrations $2\nu_2$. As a result, the contribution of the FR to the band formation increases compared to that in water. In a 70 % solution, associates with strong hydrogen bonds are not formed, but, on the contrary, the abundance of hydrophobic groups weakens hydrogen bonds (Fig. 1b). In this case, the frequency of symmetric stretching vibrations "shifts" to the high-frequency region and "moves away" from the overtone frequency of bending vibrations. As a result, the value of W and the contribution of FR to the intensity of the OH stretching band decrease in comparison with these characteristics in water and water-ethanol solution with 20 % ethanol.

2.2. Fermi resonance in NaC₈ micellar aqueous solutions

Fig. 5 a,b shows the obtained polarized and depolarized Raman spectra of aqueous solutions of sodium octanoate at different surfactant concentrations. With an increase of the sodium octanoate concentration in water, the intensity of the stretching vibration band of surfactant CH groups increases ($2800 - 3000 \text{ cm}^{-1}$) (Fig. 5). At the same time, the intensity of OH groups stretching vibrations ($2800 - 3800 \text{ cm}^{-1}$) not only decreases due to a decrease in the volume fraction of water in the solution, but also the shape of the OH band changes. The band itself shifts towards large wavenumbers (Fig. 5).

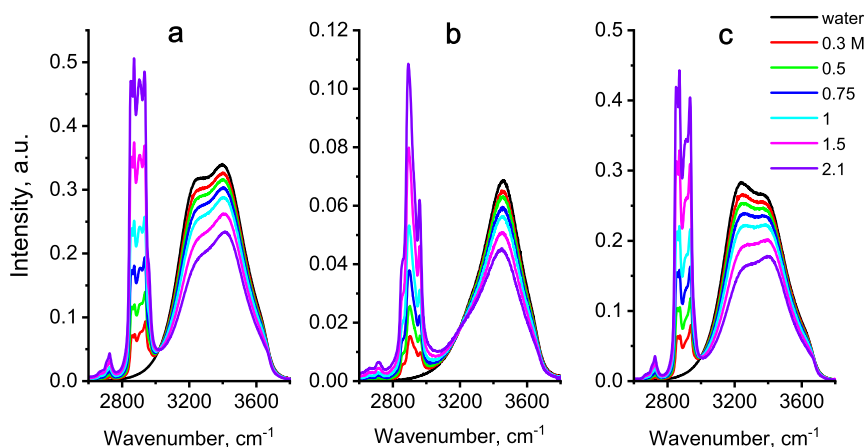


Fig. 5. Polarized (a), depolarized (b), and isotropic (c) Raman spectra of NaC_8 aqueous solutions in the range of CH and OH stretching vibrations at different surfactant concentrations

To separate the contributions of different symmetry vibrations, isotropic and anisotropic spectra were calculated using formulas (1). The obtained isotropic spectra of aqueous solutions of surfactants with different concentrations are shown in Fig. 5c.

Extraction of the Fermi doublet from the isotropic stretching band of OH groups in an aqueous surfactant solution

In order to extract the Fermi doublet from the isotropic OH groups stretching band of the aqueous surfactant solution, this band was decomposed into Gaussian components using genetic algorithms, as was done earlier for the spectra of aqueous ethanol solutions. Fig. 6a shows the decomposition of the isotropic stretching band of the water OH groups, and Fig. 6b shows the decomposition of the isotropic stretching band of the OH groups of a surfactant aqueous solution with a concentration of 1M. Due to the overlap of the stretching bands of CH- and OH-groups (see Fig. 5c), as well as for a more correct decomposition, the region from 2700 to 3050 cm^{-1} was not taken into account (Fig. 6b).

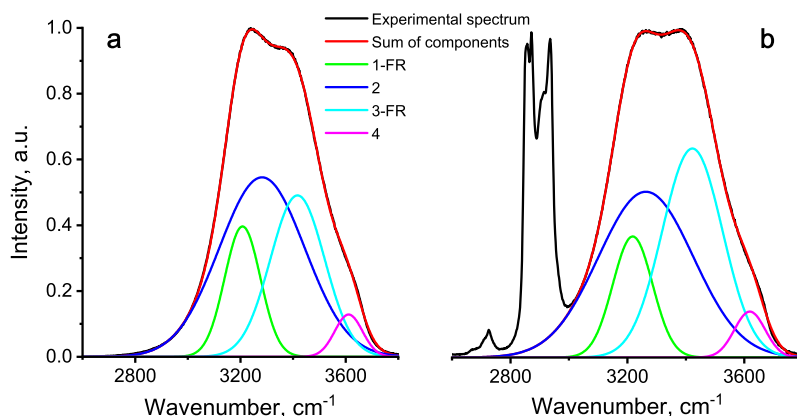


Fig. 6. Decomposition of the isotropic stretching bands of the water OH groups (a) and of the isotropic stretching bands of OH groups in aqueous solution of NaC_8 with a concentration of 1 M (b) into Gaussian components

Based on the available model conceptions of water structure, it can be assumed that components 1 and 3 in Fig. 6 are a Fermi doublet (vibrations corresponding to the bending vibration overtone and the symmetric stretching vibration with C_{2v} symmetry). Components 2 and 4 correspond to symmetric stretching vibrations with C_s symmetry and vibrations of weakly bound water molecules, respectively, which do not participate in the Fermi resonance.

The wavenumber intervals Δ between components 1 and 3 of the Fermi doublet was determined as the distance between their maxima. The values of Δ at different surfactant concentrations are presented in Tab. 2.

Table 2. Calculated interaction constants W and FR contributions to the intensity of the OH groups stretching band for aqueous solutions of NaC_8 at a temperature of 25°C (the average absolute error in determining the parameters is given in parentheses)

| Concentration NaC_8 , M | Δ , cm^{-1} ($\pm 0.21 \text{ cm}^{-1}$) | W , cm^{-1} ($\pm 0.19 \text{ cm}^{-1}$) | Contribution, % ($\pm 0.08 \%$) |
|-------------------------------------|--|---|--------------------------------------|
| 0 | 208.19 | 62.16 | 13.98 |
| 0.10 | 207.75 | 61.79 | 13.90 |
| 0.20 | 207.08 | 61.22 | 13.78 |
| 0.30 | 206.45 | 60.69 | 13.67 |
| 0.36 | 205.96 | 60.27 | 13.59 |
| 0.44 | 205.92 | 60.24 | 13.58 |
| 0.50 | 205.71 | 60.06 | 13.54 |
| 0.68 | 205.51 | 59.84 | 13.51 |
| 0.74 | 205.33 | 59.68 | 13.47 |
| 0.87 | 204.61 | 59.11 | 13.34 |
| 1.02 | 203.85 | 58.45 | 13.21 |
| 1.20 | 202.97 | 57.68 | 13.05 |
| 1.30 | 202.42 | 57.19 | 12.95 |
| 1.52 | 200.63 | 55.59 | 12.62 |
| 1.65 | 199.64 | 54.69 | 12.43 |
| 1.94 | 196.50 | 51.78 | 11.83 |
| 2.10 | 193.97 | 49.34 | 11.34 |

As can be seen from Tab. 2, before the formation of micelles (before $\text{CMC}_1 \approx 0.4 \text{ M}$), the wavenumber interval Δ decreases with increasing surfactant concentration. This is probably due to the fact that with an increase of NaC_8 concentration in the solution, the number of monomers/dimers of octanoate anions increases, which leads to a rapid weakening of hydrogen bonds between water molecules. As soon as the concentration of sodium octanoate in the solution reaches a critical value (CMC_1), with a further increase in surfactant, it becomes energetically more favorable for octanoate anions to form micelles from 15–20 ions, thereby trying to reduce (due to the hydrophobicity of surfactant hydrocarbon radicals) the surface area in contact with water. Since the surface area of the contact between water and surfactant molecules at a surfactant concentration greater than CMC_1 grows weaker than before CMC_1 , the weakening of hydrogen bonds is also insignificant: hydrogen bonds stabilize in the surfactant concentration range from 0.4 to 0.75 M (region of spherical micelles). A further increase of the surfactant concentration leads to a change in the shape of micelles (transformation into cylindrical micelles),

the area of contact between surfactant molecules and water begins to grow faster, which leads to weakening of hydrogen bonds, starting from CMC_2 , in the range of surfactant concentration from 0.8 M to 2.1 M.

Calculation of the interaction constant W and the Fermi resonance contribution to the intensity of the OH stretching band in aqueous surfactant solutions

Having determined the values of Δ from the experimental data, it is possible to calculate the FR interaction constant W and the relative contribution of the Fermi resonance to the intensity of the OH groups stretching band, as was done earlier for water-ethanol solutions.

Calculations of W and the FR contribution to the intensity of the OH band were carried out for all aqueous solutions of surfactants. The obtained values of W and the FR contribution to the intensity as a function of the surfactant concentration are presented in Tab. 2 and in Fig. 7. For water, the FR contribution was equal to 14%, which is consistent with the results obtained earlier when studying the FR in water-ethanol solutions (Tab. 1).

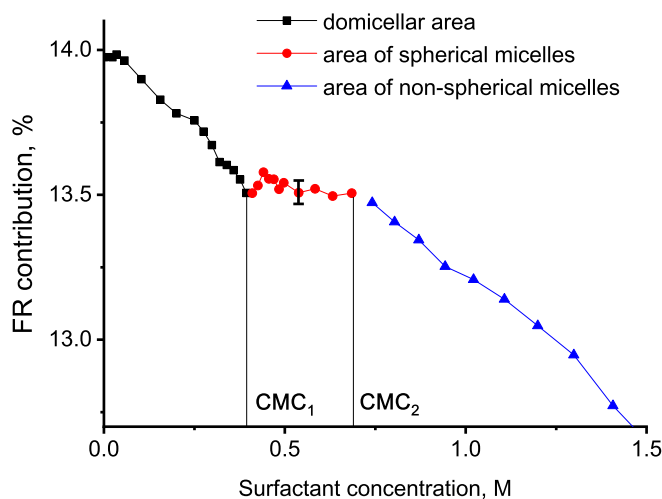


Fig. 7. Dependence of the FR contribution to the intensity of the OH stretching band on the surfactant concentration

As can be seen from Fig. 7, as the surfactant concentration increases from 0 to CMC_1 , the FR weakens and its contribution to the intensity of the OH groups stretching band decreases. Starting from CMC_1 , with the formation of spherical micelles, hydrogen bonds in water stabilize, and the FR contribution to the intensity remains constant until CMC_2 . As soon as spherical micelles begin to change their shape after CMC_2 , the FR contribution very rapidly decreases with the weakening of the hydrogen bond network.

Conclusion

Based on the analysis of the experimental Raman spectra of aqueous solutions of amphiphilic non-micelle-forming substances using optimization algorithms, quantitative estimations of the Fermi resonance (FR) contribution to the intensity of the stretching bands of the OH groups of water and water-ethanol solutions with an ethanol content of 20 vol.% and 70 vol.% were

obtained. At a temperature of 25 °C, the pointed contributions are equal: 13 % for water, 19 % for a water-ethanol solution with ethanol content of 20 vol. % and 11 % for a water-ethanol solution with ethanol content of 70 vol. % Thus, at a temperature of 25 °C, the FR contribution to the stretching band of the OH groups of water and aqueous ethanol solutions is quite large, and it should be taken into account when explaining the mechanisms of the Raman spectra formation. The FR contribution to the intensity of the stretching bands of OH groups in aqueous ethanol solutions depends on the strength of hydrogen bonds in the sample: the stronger the hydrogen bond, the more effective FR. Self-organization of amphiphilic ethanol molecules leads to an increase in FR and an increase in its contribution to the formation of the OH groups stretching band.

It was found that structural rearrangements in an aqueous solution during self-organization of micelle-forming amphiphilic compounds in it are manifested in the Raman spectrum in the region of stretching vibrations of water. The presence of a Fermi resonance between the overtone of the H–O–H bending vibration and the symmetric OH stretching vibration significantly affects the shape of the OH groups stretching band. It has been established that the contribution of FR to the intensity of the OH groups stretching band in aqueous solutions of sodium octanoate depends on the stages of surfactant self-organization. In solutions of the pre-micellar region, FR is weaker than in water. As the surfactant concentration increases up to CMC₁, FR weakens. In the range between CMC₁ and CMC₂, the contribution of the Fermi resonance remains virtually unchanged. During the transformation of spherical micelles into cylindrical and other asymmetric types of micelles, hydrogen bonds between water molecules are weakened, and the FR contribution to the formation of the OH groups stretching band drops sharply. The self-organization of surfactants in water does not significantly affect the FR contribution to the intensity of water the stretching band.

As a result of the analysis of the obtained data, it was found that the processes of formation of associates and micelles significantly affect the FR contribution to the intensity of the OH stretching band of aqueous solutions. The numerical values of the contributions for various amphiphilic compounds were calculated.

The research was carried out at the expense of the grant no. 19-11-00333 from the Russian Science Foundation, <https://rscf.ru/project/19-11-00333/>.

References

- [1] T.Bhardwaj et al., Thermo-acoustical analysis of sodium dodecyl sulfate: Fluconazole (antifungal drug) based micellar system in hydro-ethanol solutions for potential drug topical application, *J. Chem. Thermodyn. Elsevier*, **78**(2014), 1–6. DOI: 10.1016/j.jct.2014.06.003
- [2] B.-J.Kim et al., Synthesis and characterization of polyaniline nanoparticles in SDS micellar solutions, *Synth. Met. Elsevier*, **122**(2001), no. 2, 297–304. DOI: 10.1016/S0379-6779(00)00304-0
- [3] Q.Ye et al., Maternal short and medium chain fatty acids supply during early pregnancy improves embryo survival through enhancing progesterone synthesis in rats, *J. Nutr. Biochem. Elsevier*, **69**(2019), 98–107. DOI: 10.1016/j.jnutbio.2019.03.015
- [4] A.R.Elman et al., Synthesis of products labeled with the ¹³C isotope for medical diagnostics, *Russian Chemical Journal*, **57**(2013), no. 5, 3 (in Russian).

-
- [5] J.B.Rosenholm, Larsson K., Dinh-Nguyen N., A Raman spectroscopy study of micellar structures in ternary systems of water-sodium octanoate-pentanol/decanol, *J. Colloid Polym. Sci. Springer*, **255**(1977), no. 11, 1098–1109. DOI: 10.1007/BF01549896
- [6] T.A.Dolenko et al, Raman spectroscopy of micellization-induced liquid–liquid fluctuations in sodium dodecyl sulfate aqueous solutions, *J. Mol. Liq. Elsevier*, **204**(2015), 44–49. DOI: 10.1016/j.molliq.2015.01.021
- [7] M.Picquart, G.Lacrampe, Raman spectra of aqueous sodium octanoate solutions: solute and solvent study, *J. Phys. Chem. ACS Publications*, **96**(1992), no. 23, 9114–9120. DOI: 10.1021/j100202a009
- [8] I.V.Plastinin, S.A.Burikov, T.A.Dolenko, Laser diagnostics of reverse microemulsions: Influence of the size and shape of reverse micelles on the Raman spectrum on the example of water/AOT/cyclohexane system, *J. Mol. Liq.*, **325**(2021), 115153. DOI: 10.1016/j.molliq.2020.115153
- [9] I.V.Plastinin, S.A.Burikov, T.A.Dolenko, Laser diagnostics of self-organization of amphiphiles in aqueous solutions on the example of sodium octanoate, *J. Mol. Liq.*, **317**(2020), 113958. DOI: 10.1016/j.molliq.2020.113958
- [10] I.V.Plastinin et al., Features of self-organization of sodium dodecyl sulfate in water-ethanol solutions: Theory and vibrational spectroscopy, *J. Mol. Liq.*, **298**(2020), 112053. DOI: 10.1016/j.molliq.2019.112053
- [11] I.V.Plastinin et al., Manifestation of Fermi resonance in Raman spectra of micellar aqueous solutions of sodium octanoate, *Proc. SPIE 11458*, **11458**(2020), 114580V. DOI: 10.1117/12.2560462
- [12] I.V.Plastinin et al., The Role of Fermi and Darling–Dennison Resonances in the Formation of the Raman Spectra of Water and Water–Ethanol Solutions, *Bull. Russ. Acad. Sci. Phys.*, **83**(2019), no. 3, 324–329. DOI: 10.3103/S1062873819030171
- [13] A.Sokolowska, Z.Kecki, Inter-and intra-molecular coupling and Fermi resonance in the Raman spectra of liquid water, *J. Raman Spectrosc.*, **17**(1986), no. 1, 29–33. DOI: 10.1002/jrs.1250170107
- [14] A.A.Kananenka, J.L.Skinner, Fermi resonance in OH-stretch vibrational spectroscopy of liquid water and the water hexamer, *J. Chem. Phys.*, **148**(2018), no. 24, 244107. DOI: 10.1063/1.5037113
- [15] T.A.Dolenko et al., Raman Spectroscopy of Water-Ethanol Solutions: The Estimation of Hydrogen Bonding Energy and the Appearance of Clathrate-like Structures in Solutions, *J. Phys. Chem. A*, **119**(2015), no. 44, 10806–10815. DOI: 10.1021/acs.jpca.5b06678
- [16] E.Blanco et al., A comparative study of the physicochemical properties of perfluorinated and hydrogenated amphiphiles, *J. Colloid Interface Sci.*, **288**(2005), no. 1, 247–260. DOI: 10.1016/j.jcis.2005.02.085
- [17] A.Gonzalez-Perez et al., Thermodynamics of self-assembly of sodium octanoate: Comparison with a fully fluorinated counterpart, *Mol. Phys.*, **101**(2003), no. 21, 3185–3195. DOI: 10.1080/00268970310001620177

- [18] M.F.Vuks, L.V.Shurupova, Light scattering and phase transitions in aqueous solutions of simple alcohols, *Optics and spectroscopy*, **40**(1976), no. 1, 154–159 (in Russian).
- [19] L.V.Shurupova, Some Features of the Temperature Behavior of Additional Scattered Light Peaks, *Vestnik SPbGU*, **4**(1994), no. 25, 16–25 (in Russian).
- [20] K.Takaizumi, T.Wakabayashi, The freezing process in methanol-, ethanol-, and propanol-water systems as revealed by differential scanning calorimetry, *J. Solution Chem.*, **26**(1997), no. 10, 927–939. DOI: 10.1007/BF02768051
- [21] K.Takaizumi, A Curious Phenomenon in the Freezing–Thawing Process of Aqueous Ethanol Solution, *J. Solution Chem.*, **34**(2005), no. 5, 597–612. DOI: 10.1007/s10953-005-5595-6
- [22] Y.M.Zelenin, Effect of Pressure on Clathrate Formation in a Water–Ethanol System, *J. Struct. Chem.*, **44**(2003), no. 44, 130–136. DOI: 10.1023/A:1024993200295
- [23] S.Burikov et al., Raman and IR spectroscopy research on hydrogen bonding in water–ethanol systems, *Mol. Phys.*, **108**(2010), no. 18, 2427–2436. DOI: 10.1080/00268976.2010.516277
- [24] M.H.Brooker, O.F.Nielsen, Praestgaard E., Assessment of correction procedures for reduction of Raman spectra, *J. Raman Spectrosc.*, **19**(1988), no. 2, 71–78. DOI: 10.1002/jrs.1250190202
- [25] M.P.Lisitsa, A.M.Yaremko, Fermi Resonance, *Kyiv, Naukova Dumka*, (1984) (in Russian).
- [26] I.V.Plastinin et al., Contribution of Fermi and Darling–Dennison resonances to the formation of Raman spectra of water and water–ethanol solutions, *J. Raman Spectrosc.*, **48**(2017), no. 9, 1235–1242. DOI: 10.1002/jrs.5207
- [27] R.Lemus et al., Spectroscopic Description of H₂O in the su(2) Vibron Model Approximation, *J. Mol. Spectrosc.*, **214**(2002), no. 1, 52–68. DOI: 10.1006/jmsp.2002.8571
- [28] A.D.Bykov, K.V.Kalinin, Calculation of vibrational energy levels of water molecule by summing divergent perturbation theory series, *Opt. Spectrosc.*, **111**(2011), no. 3, 367. DOI: 10.1134/S0030400X11080091
- [29] S.V.Krasnoshchekov, E.V.Isayeva, N.F.Stepanov, Criteria for first- and second-order vibrational resonances and correct evaluation of the Darling–Dennison resonance coefficients using the canonical Van Vleck perturbation theory, *J. Chem. Phys.*, **141**(2014), no. 23, 234114. DOI: 10.1063/1.4903927

Влияние самоорганизации амфифильных соединений на вклад резонанса Ферми в формирование валентной полосы ОН-групп

Иван В. Пластинин

Татьяна А. Доленко

Сергей А. Буриков

Научно-исследовательский институт ядерной физики имени Д. В. Скобельцына

Московский государственный университет имени М. В. Ломоносова

Физический факультет

Московский государственный университет имени М. В. Ломоносова

Москва, Российская Федерация

Сергей А. Доленко

Научно-исследовательский институт ядерной физики имени Д. В. Скобельцына

Московский государственный университет имени М. В. Ломоносова

Москва, Российская Федерация

Аннотация. Исследована роль резонанса Ферми (РФ) в формировании валентной полосы ОН-групп спектров комбинационного рассеяния (КР) водных растворов амфифильных соединений с разной длиной углеводородных радикалов: этанола и октаноата натрия. Обнаружено влияние процессов самоорганизации амфифилов на вклад РФ в интенсивность валентной полосы ОН водных растворов.

Ключевые слова: амфифильные вещества, самоорганизация, резонанс Ферми, водные растворы, спектроскопия комбинационного рассеяния, генетические алгоритмы.