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SIZE EFFECT AT NANOMETRIC SCALE BASED ON SPECTRAL MEASUREMENTS ON WATER IN OIL MICROEMULSIONS

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Această lucrare propune metode clasice, cum sunt spectroscopia şi conductometria, cunoscute ca instrumente specifice de caracterizare fizico-chimică a materialelor la nivel macroscopic, ca tehnici alternative şi complementare pentru analiza structurii fluidelor la scară nanometrică. Astfel, spectroscopia VIS a fost aplicată pentru localizarea colorantului în agregatele coloidale formate prin auto-asamblarea moleculelor de surfactant la interfaţa apă/ulei, precum şi pentru evaluarea polarităţii locale. Măsurătorile spectrale şi de conductivitate permit definirea naturii fizico-chimice a acestor agregate şi, prin urmare, alegerea compoziţiei adecvate pentru sinteza de nanostructuri, controlul naturii, formei şi dimensiunii lor. Au fost preparate şi caracterizate prin spectroscopie VIS, imprăştierea dinamică a luminii şi conductometrie, microemulsii de tip apă în ulei (W/O), diametrul agregatelor coloidale fiind estimat pe baza deplasărilor maximelor de absorbtie ale spectrelor electronice asociate efectului de dimensiune şi confirmat prin măsurători de imprăstiere dinamică a luminii.

This paper proposes some classical methods, as spectroscopy and conductometry, known as specific instruments for physico-chemical characterization of materials at macroscopic level, as alternative and complementary techniques for fluid structure investigation at nanoscale level. Thus, the VIS spectroscopy has been applied for dye location into the colloidal aggregates formed by self-assembling surfactant molecules at water/oil interface and for local polarity evaluation. Spectral and conductivity measurements allow to assess the physico-chemical nature of these aggregates and therefore the proper compositions for nanostructures synthesis and to control their nature, shape and size. The water in oil (W/O) microemulsions have been prepared, the diameter of colloidal aggregates being estimated on base of the size effect revealed by their electronic spectra and confirmed by Dynamic Light Scattering measurements.

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1. Introduction

Materials with nanoscopic dimensions such as quantum dots, nanorods, nanowires and nanotubes, have attracted recently a great attention due to their intriguing properties that cannot be obtained from the conventional macroscopic (bulk) materials. These novel nanoscale materials are expected to have potential applications in areas such as optoelectronic device technology, photocatalyst fabrication and drug delivery systems [1-3]. The unique characteristics of the nanomaterials are believed to be originated in quantum confinement effects due to the narrowing of band structure into discrete quantum levels as a result of limited size of the particles [4].

There is a continuing and growing need for techniques to determine characteristics of particles in science, industry and environment. Optical methods are among the most powerful being capable of rapid *on-line* and *in-situ* measurements. The light scattering methods are used in a wide spectrum of fundamental and applied optical problems, including evaluation of materials properties in chemical and materials science as well as in technological processes.

Dynamic Light Scattering (DLS) is one of the most popular experimental techniques used in characterization of complex liquids: colloidal suspensions, polymer solutions, polymer melts, gels [5–8]. Dynamic Light Scattering is particularly useful in sensing the presence of very small amounts of aggregated polymers or proteins and studying samples containing a very large range of particle masses. It can be quite valuable for real-time monitoring of size changes. DLS uses the scattered light to measure the rate of particle diffusion. The motion data are conventionally processed to derive a size distribution, where the size is given by the “Stokes radius” or “hydrodynamic radius” of the particle. This hydrodynamic size depends on both mass and shape (conformation).

Ultraviolet – Visible transmission spectroscopy appeared more than five decades ago [9, 10] and has re-gained the interest of the process industry [11, 12], due to recent advances in the algorithms using inverse-solution methods [13] and the increase and reliability of equipment. A modern spectrometer enables the acquisition of the complete ultraviolet–visible-near infrared (UV–VIS–NIR) spectra with excellent wavelength resolution and short measurement times. The information is obtained from spectroscopy analysis of a sample measured over a broad range of wavelength (190–820 nm), and/or with the scattered light measured at one or several observation angles. Thus, an analysis of particles population may be possible with sizes ranging from nanometers to micrometers [14–19]. Systematic spectroscopy study over the range of wavelengths 190–820 nm and analysis of emulsions, in terms of droplets size distribution in the spectral region (300–820 nm), have been successfully performed and applied to the continuous estimation of the droplet size distribution (DSD), and to the assessment of stability of emulsions [16–22].

Microemulsions are thermodynamically stable isotropic clear dispersions consisted in oil, water, and surfactant (and/or cosurfactant) mixtures [23]. The presence of domains of different polarity in the colloidal assemblies (O/W, W/O, bicontinuous, etc.) helps these templates to solubilize moieties of different solubilities. Consequently, microemulsions have the potential advantages of high solubilization capacity, penetration enhancements, high stability, and ease of preparation [24]. In addition to single-phase microemulsions, several phase equilibria are known, namely Winsor systems [25]. A Winsor I (WI) system consists of the O/W microemulsion (direct micells) which is in equilibrium with an excess oil phase, while a Winsor II (WII) system is a W/O microemulsion (reverse micelles) which is in equlibrium with an excess aqueous phase. The Winsor III (WIII) system is a bicontinuous microemulsion, while a macroscopically single-phase microemulsion is denoted as a Winsor IV (WIV) system [26].

Water-in-oil (W/O) microemulsion is a well-suitable confined reacting medium for the synthesis of structured functional inorganic nanoparticles of controlled size and shape [27]. This is a quite new procedure, which allows preparation of ultrafine mono size and shape nanoparticles within the size range of the particle diameter (L): 5–50 nm and can offer highly promising and novel options for a wide range of applications in optics, microelectronics, catalytic systems, chemical nanosensors and medical field [28].

Visible spectroscopy (VIS) has also been used as a powerful tool to obtain information on the compositional, structural and dynamic characteristics of the colloidal aggregates by using a dye as VIS molecular probe [29]. Moreover, in this work, the VIS spectroscopic technique is originally exploited for the evaluation of the size effect and the estimation of the dimensions of the nanoparticles found in the organized systems.

This study is focussed on the following aspects: i) preparation of different microemulsion systems and characterization by using spectral methods and conductivity measurements; ii) control of nature, size and shape of colloidal aggregates (water or oil droplets) templated by microemulsion systems based on size effect revealed on VIS spectra and DLS measurements; iii) highlighting the size effect both in microemulsions and solid nanoparticles.

2. Experimental

All chemicals were of the highest purity available and were used as received without further purification or distillation: *n*-heptane from CHROMASOLV®, Brij 30 (polyoxyethylene 4-lauryl ether) and TEG (triethylene glycol) provided by SIGMA®, nickel (II), nitrate, hexahydrate and ammonia solution 25% (NH_4OH) from MERCK and bromthymol blue (BTB) was from Chemopal. Ultra-pure water (Millipore Corporation) was used.

A series of working solutions have been used: solutions of dye in water, surfactant and n-heptane, respectively, aqueous solutions of surfactant and surfactant/dye mixture, respectively with concentrations in the range of 0.032–4.2 mM. As micellar systems water/ Brij/ BTB were used, and water/ Brij (25%)/ BTB/ heptane microemulsion systems were prepared and tested.

DLS measurements were performed on Malvern Nanosizer equipment. Electronic spectra were recorded by UV–VIS–NIR spectrophotometer type V570, Jasco. For the conductivity measurements, a Consort C831 multi-parameter analyser was used.

3. Results and discussion

In order to reveal the dynamic and structural effect of micelles and microemulsions systems by spectral methods bromthymol blue (BTB) dye is used as molecular VIS probe. Molecular probe technique uses the molecular absorption UV – VIS probes in order to study the dynamic, structural and size effect in micelles, reverse micelles and microemulsions. Two main criteria have been used to choose the BTB as molecular probe for spectral study in micelle and microemulsion systems: i) it exhibits *solvatochromic effect*, meaning that the electronic spectra of the probe must have absorption peaks well defined in UV – VIS domains for all the components of the studied systems; ii) it has not *tensioactive properties*, both in molecular and in the aggregate systems (aggregates between its own molecules or to the surfactant molecules) [23].

3.1. Solvathocromic behaviour of BTB in different media

The electronic transition energy of the probe molecules, as reflected in the wavelength of their absorption maxima λ_{max}, provides information on the *polarity* of the microenvironment. Firstly, in order to unveil the preferential location of BTB in micelles and microemulsion solutions, their spectra have been *calibrated* by placing the probes into well-established environments.

Table 1

Spectral parameters of BTB in different solvents

Solvent	λ, nm
Water	430
TEG	416
Brij 30	408

The wavelength of their absorption maxima, λ_{max}, in VIS are indicated in Table 1. In addition, the relative solubility in different media also provides information on their possible locations. The molecular probe, BTB, is almost insoluble in both solvents used: water and heptane.

The spectral parameters of BTB solutions are specific for each studied system: aqueous, oxyethylene (Brij 30) and triethylene (TEG) glycol, fact that justifies the choosing of BTB as molecular VIS probe for structural investigations in ternary systems: water/ Brij/ heptane.

3.2. Dynamic and structural effects in binary water/ Brij systems

By measuring the absorption maxima shifts on the electronic spectra of water/ Brij/ BTB systems at different surfactant concentrations the critical micellar concentration (CMC) has been determined (Fig. 1).

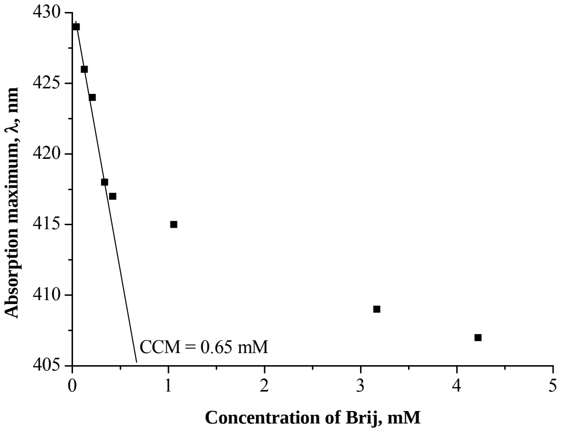

Fig. 1. Dependence of absorption maxima wavelength for BTB on the concentration of the surfactant in water/ Brij/ BTB systems

The spectrophotometric method consists in determining the wavelengths of the absorption maxima for every composition and plotting them versus the surfactant concentration. The CCM corresponds to the point where the slope is changed. The λ_{max} values of the spectra are presented in Fig. 1.

The spectra obtained in solutions with concentration below CMC exhibit the same absorption maxima as in pure aqueous solutions. By raising the surfactant concentration over CMC, when the number of micelle aggregates with nonpolar core is growing, the absorption maxima shift hipsochromic, suggesting a decrease in the polarity of the media. One can be seen that the absorption maxima wavelength depend on the surfactant concentration.

Also, one is worth to notice that the obtained CMC is about 0.600mM, a similar value with that obtained by stalagmometric method [23]. It results that the spectroscopic method is a convenient technique for such experiments.

3.3. Compositional, dynamic and structural effects in ternary water/ Brij/ heptane system

A major motivation for this research is the challenge to understand how ordered or complex structures form spontaneously by self – assembly, and how such processes can be controlled in order to prepare structures with predefined geometry and, as a consequence, predetermined properties.

3.3.1. Construction of phase diagram

The obtaining and using of microemulsion of any type, and consequently the nanostructure corresponding to specific applications, requires the delimitation of the interest regions for water/surfactant/oil system by drawing the appropriate phase diagrams.

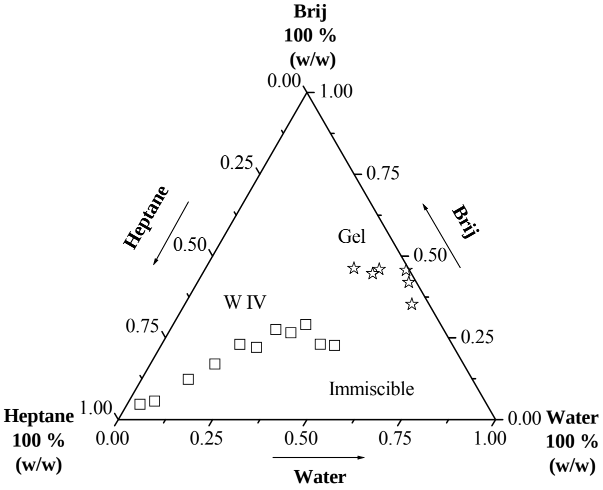

Fig. 2. Ternary phase diagram of the system water /Brij/ heptane at room temperature

In order to find out the region where microemulsion can be formed, ternary phase diagram was constructed using surfactant titration method at room temperature (Fig. 2) following the procedure previously described [30].

The left side of the diagram corresponds to an organic solution of surfactant, the water being present only in small amounts, corresponding to a system of reverse micelles (RM). The right side of the diagram corresponds to an aqueous surfactant gel containing small amounts of heptane. The solubilisation of water and heptane, respectively in heptane/aqueous solution, increases proportionally with the surfactant concentration for a given water/oil volumetric ratio, $R = V_W/V_O$.

3.3.2. Localisation of BTB at W/O interface by spectral measurements

The effect of successive additions of water on the microenvironment of micelles formed in the water /Brij/ heptane was studied. The surfactant solutions were prepared by dissolving the surfactant in the organic solvent, mentioned above (30% of Brij and 70% of heptane). Different amounts of water, denoted by $R = V_W/V_O$, were added to these solutions and the resulting samples were mechanically stirred for few minutes. Finally, the VIS electronic spectra were registered; the corresponding absorption maxima wavelengths depending on added water amounts, $R = V_W/V_O$ are presented in Fig. 3.

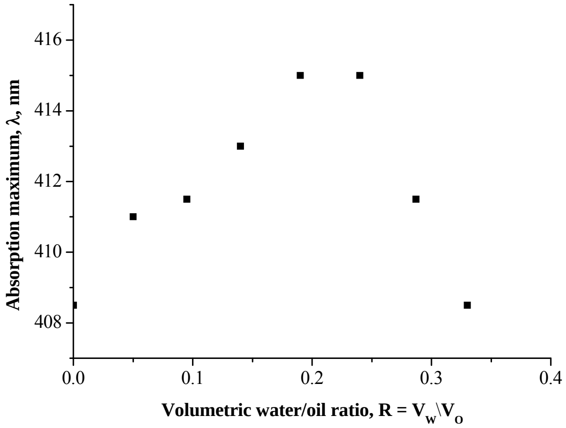

Fig. 3. Dependence of absorption maxima wavelength on increasing water content of microemulsions

One can be concluded from this behaviour that Brij molecules self assemble at water/oil interface by stabilizing the water droplets dispersed into heptane phase, corresponding to the W/O microemulsion systems; this explains the shift of the wavelengths to the absorption maximum of BTB in Brij (408 nm). Here, the increase of the wavelength corresponding to the absorption maximum in TEG is due to the hydration of the oxyethylene groups of surfactant molecules. The shift to lower energies (Fig. 3), for water/oil volumetric ratios between 0.2 and 0.3, might be associated to the phase separation into O/W microemulsion in equilibrium with oil excess phase, corresponding to WI system.

Finally, one can affirm that the BTB is located at the oxyethylene groups, what means that dye molecules are solubilized into the colloidal aggregates core, when W/O microemulsion is formed. When the phase separation occurs and the WI system is formed, the BTB molecules are simple associated to the surfactant molecules and solubilized into the heptane excess phase.

3.3.3. Identification of phase inversion point of ternary water/ Brij/ heptane system

The phase diagrams permit a rigorous selection of the optimal composition to carry out the applications in microemulsion depending on surfactant self – assembling at water/heptane interface. More precisely, if the process occurs in a polar, aqueous medium, the zones of interest are Winsor II (W/O, W) and Winsor IV (W/O), while in a nonpolar, organic medium, the zones are Winsor I (O/W, O) and Winsor IV (O/W).

In order to characterize the systems containing water nanodroplets dispersed into the oil phase (W/O) several WIV microemulsion of different compositions were prepared (Table 2) and characterized by VIS spectroscopy (Fig. 4) and electrical conductivity measurements (Fig. 5).

Table 2

Compositions of the tested W IV microemulsions with various water/oil volumetric ratios, R

R	0.03	0.05	0.11	0.18	0.25	0.33	0.43	0.54	0.67	0.82	1.00
Brij % (w/w)	4.7	5.7	12.3	17.0	23.0	22.1	27.5	26.5	29.0	23.1	22.7
Water % (w/w)	3.4	6.8	12.4	17.1	20.7	25.6	28.0	32.5	35.2	42.0	46.0
Heptane % (w/w)	91.9	87.5	75.3	65.9	56.3	52.3	44.5	41.0	35.8	34.9	31.3

From Fig. 4 one can observe that the wavelengths increase starting from the absorption maxima of the BTB in Brij (λ_{max} = 408 nm) to that in TEG (λ_{max} = 416 nm). This suggests the hydration of the oxyethylene groups and consequently the formation of W/O microemulsion. By increasing the water content, $R = V_W/V_O \sim 0.3$, the repulsive forces between oxyethylene groups of surfactant molecules become predominant and the wavelength shifts to the absorption maxima of the BTB in Brij (λ_{max} = 408 nm) are observed (Fig. 4). This hipsocromic effect is associated to phase inversion point when the O/W microemulsion occurs and a mixture of W/O and O/W microemulsions is formed.

To conclude, the BTB molecules are in both cases solubilised into the colloidal aggregates core, as they are almost insoluble in any of these two solvents, water and heptane, when the surfactant is absent.

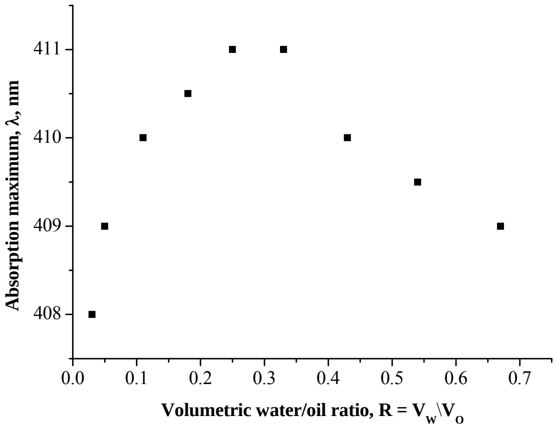

Fig. 4. Dependence of the absorption maxima wavelength on the water/oil volumetric ratio, R

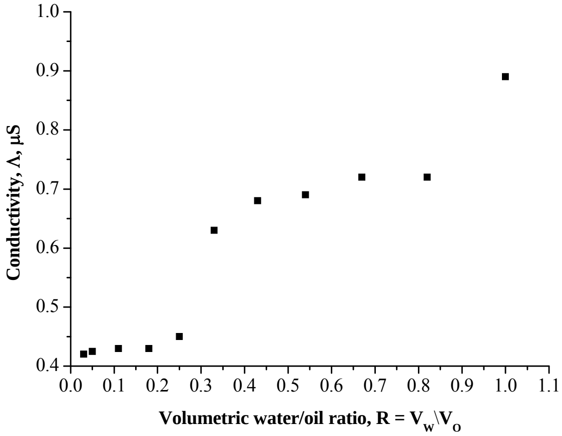

Fig. 5. Electrical conductivity dependence on the water/oil volumetric ratio, R

The phase inversion point at $R = V_W/V_O \sim 0.3$ can be also assigned to the slope change in conductivity values on the volumetric water/oil ratio (Fig. 5), which is in quite good agreement with spectral measurements.

3.4. Size effect on fluid nanostructures and templated solid nanoparticles

The nanostructures characteristics have length scale in the low nanometer range that influences their physical or chemical properties. Their novel or unusual physical properties are mainly due to finite-size effect: electronic bands are gradually converted to molecular orbital as the size decreases.

The difference in the peak position of electronic spectra would relate to the size effect of nanostructured units in the bulk phase. When a three-dimensional square-well potential with the length of L in x, y and z directions is of the quantum size, the energy of an electron, ΔE, confined within potential, well can be given by the following equation [31]:

$$\Delta E = \frac{3 \cdot \hbar^2 \cdot \pi^2}{2 \cdot m \cdot L^2}, \ \hbar = \frac{h}{2\pi} \tag{1}$$

where m is the static mass of an electron ($9.10938 \cdot 10^{-31}$ Kg), and h is the Planck constant ($6.62608 \cdot 10^{-34}$ J·s).

3.4.1. Size estimation of different W/O droplets

Since the phase inversion point is around R = 0.3, and W/O microemulsions are involved in inorganic nanoparticles preparation, several compositions, corresponding of different water/surfactant mass ratio, $r = W_W/W_{Brij}$ have been prepared (Table 3). These microemulsions have been further used to determine the size of the water droplets dispersed into the heptane liquid phase in order to establish if their size could be controlled by changing the concentration of the surfactant.

Table 3

Size estimation based on VIS and DLS spectra of W/O microemulsions

$r = W_W/W_{Brij}$	0.06	0.13	0.15	0.19	0.26	0.37	0.56	0.72	1.19
L_{VIS} nm (VIS spectra)	4.0	5.0	5.3	6	6.5	7.8	10.2	12.5	17.7
L_{DLS} nm (DLS spectra)	4.3	5.1	5.5	5.9	6.7	7.5	9.8	11.9	17.5
Polydispersity	0.113	0.109	0.214	0.203	0.195	0.201	0.254	0.179	0.158

The size of the aggregates in micelles, L, may be obtained from ΔE (equation 1) which is the difference between the spectral position of BTB peak in

TEG (hydrated oxyethylene groups) (416 nm) and that in microemulsions (Table 3). The results obtained from VIS spectra are sustained by the DLS measurements and follow the size dependence of water/surfactant mass ratio, r [32].

3.4.2. Size estimation of $Ni(OH)_2$ solid nanoparticles dispersed in different W/O droplets

In order to prepare NiO nanoparticles of different size (4 to 7 nm) several microemulsions corresponding to four water/surfactant mass ratios have been prepared (Table 4).

Table 4

Size estimation based on VIS and DLS spectra of $Ni(OH)_2$ solid nanoparticles

Systems	$r = W_W/W_{Brij}$	0.06	0.13	0.15	0.26
Ni^{2+}/Brij/heptane	L_{DLS} nm	4.5	5.1	5.6	6.6
	Polydispersity	0.103	0.195	0.265	0.224
$Ni(OH)_2$/Brij/heptane	L_{DLS} nm	6.0	7	7.5	8.3
	Polydispersity	0.213	0.149	0.205	0.284
	λ_{max} nm	624.5	628	629.5	630.5
	L_{VIS} nm	5.9	7.2	8.1	9.0

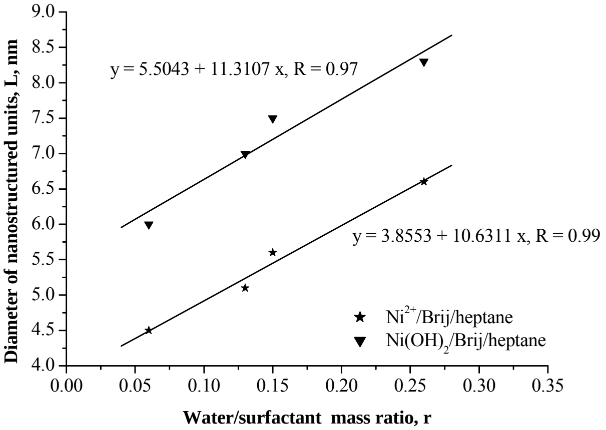

Fig. 6. Size dependence on water/surfactant mass ratio for W/O microemulsions containing solubilized Ni^{2+} salt and $Ni(OH)_2$ respectively

One can be observed that the diameter of both nanostructured units increased linearly with the masic water/surfactant ratio (Fig. 6), and the size of

W/O nanodroplets solubilizing Ni^{2+} salt (Ni^{2+}/Brij/heptane) is lower than that of containing $Ni(OH)_2$ nanoparticles ($Ni(OH)_2$/Brij/heptane) of about 1.6 nm. This significant difference can also be estimated by subtracting the two intercepts, as the equations slopes are not very different and this can be associated to $Ni(OH)_2$ formation into the w/o nanodroplets.

The final material, NiO nanoparticles, prepared into the microemulsion composition corresponding to $r = 0.13$, was obtained by breaking the microemulsion and calcinations, by following a procedure detailed elsewhere. The NiO nanoparticles size estimated from HR-TEM measurements was about 5 nm, a value that is in a good agreement with the predesigned material by using microemulsion template and controlling it by spectral and conductivity methods [33].

4. Conclusion

The results show that Bromthymol Blue (BTB) is an effective VIS molecular probe that proved to have specificity regarding this spectroscopy domain and good affinity versus nonionic surfactants. These properties allow drawing the phase diagram and obtaining information on composition, structural and dynamic characteristics of assembled structures in colloidal systems.

The solubility of BTB molecular probe in selected media, determined by UV-VIS absorption spectroscopy, provides useful information regarding the possible location in micelle systems and later in microemulsion. The study of selected systems is useful for understanding the association phenomena with the phase transitions, like: i) oil (heptane) solubilisation in aqueous solution of surfactant; ii) water solubilisation in oil solution of surfactant; also the type, phase inversion point, and the stability of micro emulsion may be determined. This tehnique is also appropriate to put in evidence the size effect based on spectral shifts, respectively to estimate the nanostructure size obtained by self-assembly method.

The electrical conductivity measurements can also be used to obtain information about the type of colloidal aggregates based on very different values of conductivity of aqueous and organic media.

W/O microemulsions have been used in order to prepare monodispersed, reproducible and stable nanostructures, W/O droplets and $Ni(OH)_2$ nanoparticles with tailored shape and size based on spectral and conductivity measurements.

One can be concluded that the classical methods, VIS spectroscopy and conductivity measurements, combined with DLS technique, could be considered as reliable procedures both to characterize nanostructures avoiding very expensive techniques as microscopy, X-ray etc. and to design the properties of final materials by controlling the features of microemulsion templates.

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