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STUDY ON SOLUBILITY OF SURFACTANTS IN WATER BY FIBER OPTIC SPECTROPHOTOMETER

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Abstract. The vegetable oil based emulsifiers represent a remarkable potential in the petroleum industry. In the chemical enhanced oil recovery (EOR) the application of the nonionic surfactants have a growing importance as a biodegradable type additive. The aim of our work is to prepare a simple and rapid instrumental measurement that could be used in the industrial practice and would be suitable to control the water solubility of the surfactants produced for EOR technologies by using of the available AvaSpec fiber optic spectrophotometer.

Keywords: surfactant, solubility, spectrophotometer, HLB value.

1. Introduction

Nowadays, as a result of the growing tendencies towards environmental consciousness, the biodegradable and environmentally friendly vegetable oil based surfactants are going to come into view in more and more areas. Mainly they include the vegetable oil based nonionic surfactants, which are widely applied in several industries. Different types of them are used in the cosmetic- and household chemicals industry, as well as in significant amounts in the petroleum industry. They are used within the petroleum industry also in the production of emulsion type motor fuels. On the other hand the vegetable oil based emulsifiers represent a remarkable potential also in the area of production of easy-dissolvent and environment-friendly metalworking lubricants. Moreover, in the enhanced oil recovery (EOR) the usage of the nonionic surfactants has a growing importance in the petroleum industry [1].

In case of the nonionic surfactants, due to their amphipathic nature, one of the most important characteristics of the molecule is the solubility in water and also in crude oil. Thus to choose the appropriate utilization area, it is important to determine these properties [2].

Despite many advantages of vegetable oil based nonionic surfactants, their major discommodities are vegetable oils and fatty acids, as well as the esters gained from them, having multiple components. Also their composition largely depends on their raw materials and the production process. The presence of unconverted raw materials and the nascent byproducts could also affect surfactant solubility, so it is essential to take this into consideration under examination of solubility of these types of components. The literature is deficient in the topic of practical determination of solubility, thus it became necessary to develop a new test method which would be more suitable to characterize the extent of solubility than the earlier ones [3-5].

The aim of our work is to prepare a simple and rapid instrumental measurement that could be used in the industrial practice and would be suitable to control the water solubility of the surfactants produced for EOR technologies, and hence to ensure the reproducibility of their quality.

2. Experimental

The Pannon University, Institute of Chemical and Process Engineering, Department of MOL – Hydrocarbon and Coal Processing since many years has been running an intensive research on development of new surfactants for various purposes. In order to qualify the own-developed surfactants, new examination methods were needed to evolve. As the part of this research the demand of a reliable measurement of the surfactant solubility in water came into view. It was examined whether the available AvaSpec fiber optic spectrophotometer is capable to characterize the solubility of the surfactants in water.

Table 1

Characteristics of the experimental fatty acid-alkanolamine esters

	SE-1	SE-2	SE-3	SE-4	SE-5	SE-6
KV, mm^2/s	19.20	18.27	18.62	20.58	19.30	20.90
Acid number, mg KOH/g	5.4	4.6	4.6	4.2	1.7	2.7
Saponification number, mg KOH/g	116.8	138.1	139.2	134.2	141.4	134.2
Hydrophilic-lipophilic balance (HLB*)	18	17.3	16	14.8	19.4	18.3
Appearance	clear	clear	clear	clear	clear	clear

* The data were calculated by a method based on the determination of the water number

Based on the data it could be concluded that the HLB values of the examined surfactants were extremely high, because the HLB method was developed from fatty acid-polyethylene glycol ester type surfactant. It follows from the fact that the chemical structure and solubility of these surfactants were remarkably different from that fatty acid-polyethylene glycol ester type surfactant family used as a basis for the definition of the HLB value based on the calculation method known by literature [6].

In the experimental work an AvaSpec 2048 Standard fiber optic spectrophotometer (Fig. 1) with AvaLight-DHc Compact Halogenlight source (Fig. 2) was applied.

Fig. 1. AvaSpec 2048 Standard

Fig. 2. AvaLight-DHc Compact Halogenlight source Spectrophotometer

The characteristics of the spectrophotometer:

– Optical level; Symmetric Czerny-Turner, 75 mm focal length
– Wavelength range; 200–1100 nm
– Resolution; 0.04–20 nm
– Detector; CCD linear, 2048 pixels

The characteristics of the light source:

– Wavelength range: 200–2500 nm
– Stability; <1 mAU
– Optical performance (in fiber); 7 μW
– Temperature range; 278–308 K

Based on the measurements the light transmitting abilities of the distilled water solutions for all surfactants in the concentration of 0.1; 0.2; 0.5; 1, 2 and 5 mas % were determined. The measurements were done at 293 K and 410 nm wavelength. The flexible applicability was obtained by the advantages of the fiber optic instrument and only 50 cm^3 surfactant solution was sufficient and additional the examination could be carried out also in a simple beaker.

3. Results and Discussion

To characterize the solubility of nonionic surfactants in water with the transmittance values, the measurements were carried out by the spectrophotometer. The solubility of the surfactants in water was investigated in the function of concentration of the SE-1 marked surfactant (Fig. 3).

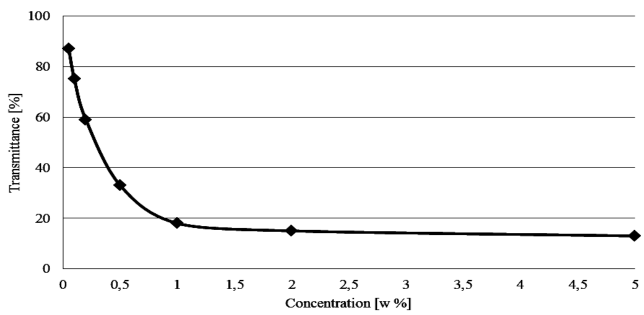

Fig. 3. Solubility of the SE-1 marked surfactant in water plotted *vs.* its concentration

It was observed that because of the growing surfactant concentration the number of the insoluble, light absorbing particles in the liquid increased, in the meantime the light transmission capability of the evolving emulsion nonlinearly decreased. On the other hand it is well known that the light transmission capability is influenced by the light absorbance of the nano-dispersed particles and the solvated surfactant molecules as well as the size of micelles, and also their light scattering. In this work the influencing effect of light transmission capability of dispersed, insoluble particles and the correlation between the characteristics of the particle size and the transmittance were examined.

Additionally the different types of solubility of the surfactants in the function of different particle size distribution in water were also studied.

The particle size distribution of the disperse systems was analyzed by using the solution of 1 m/m % surfactant containing filtered water from a Hungarian reservoir at 353 K. Before the tests, the solutions were heat-treated and also ultrasonic treatment was applied, aiming the suitable scaled dissolution of the surfactants. For the particle size analysis a Zetasizer device was applied, manufactured by Malvern company and operated by the dynamic light scattering method (DLS). By this device the particle size can be detected from 1 nm to 5 µm. The concentration of the examined surfactant was 0.5 % – relatively to the practical application and above the *cmc* (critical micelle concentration) of these surfactants.

To separate the two effects influencing the transmittance and to measure the rate and the ratio of the absorbance affected by the surfactant solution two sets of experiments were prepared:

- to examine the absorbance of the perfectly soluble particles
- to study the increasing effect of the absorbance caused by the insoluble particles.

For the measurement fatty acid-diethanolamine esters were selected, which were completely dissolved in water without turbidity. Another series of surfactants were used with the same chemical structure but limited solubility in water, which members had insoluble average particle sizes in a wide range. The applied surfactant concentration was 0.5 m/m % where the negligible differences between the dissolved surfactant concentration influenced the light transmittance capability less than the differences between the average sizes of the insoluble particles.

In the tested colloidal size range (50–350 nm) the light transmission only negligibly depends on the average size of the micelles and differences between the molar absorbances of the surfactants (Fig. 4).

Based on the results only the mild reduction of the transmittance with the increased particle sizes of the surfactants dispersed in water was observed. At the 0.5 % concentration of the surfactants the degree of solubility was even over 75 % of the transmittance. It is known that the nonionic surfactants are usually used as mixtures in petroleum industry; it was found that the gained solubility data could be suitable for comparative assessment. The concentration that belongs to 50 % value of transmittance was also chosen, which is showed by Fig. 5. The determination of the 50 % limit value was based on application aspects.

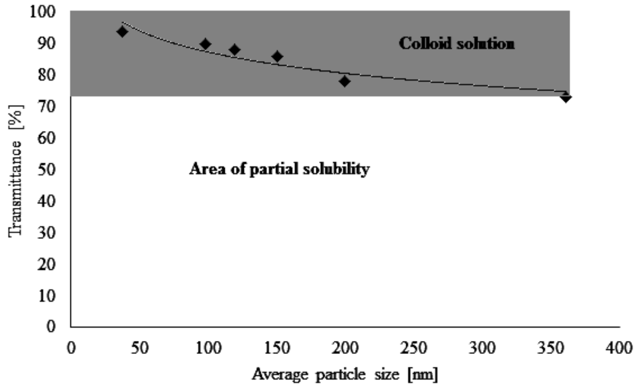

Fig. 4. The correlation between the transmittance and the average particle size of dispersed surfactants in water

In case of the usage of surfactants in solutions there is often an essential requirement that the aqueous solution has to be transparent. Above the concentration of 50 % the transmittance depending on the light absorption is mainly determined by the concentration of the dissolved surfactants and less emphatic by the number and size of the *non*solved particles in the emulsions. The solutions having more than 75 % of light-transmission capability have only slightly opaque and transparent appearance and they not contain the turbidity causing particles having an average size of the soluble micelles larger than 350 nm in a significant concentration.

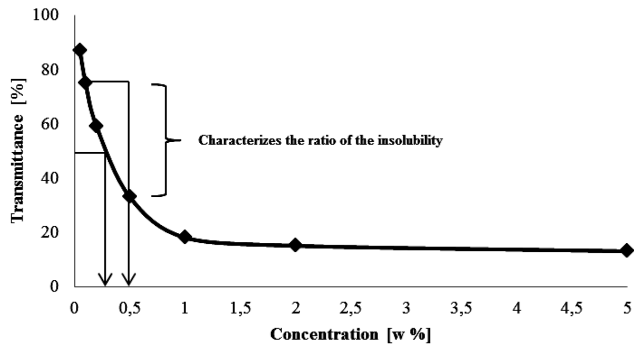

Fig. 5. The relationship between the transmittance and the surfactant concentration

The results of the partial solubility and values of their repeatability are shown in Table 2.

Table 2

Results of partial solubility values and their repeatability

Symbol of the surfactant	Average, %	SD, %	RSD, %
SE-1	72.1	1.38	1.52
SE-2	50.3	0.65	0.83
SE-3	62.3	2.35	3.21
SE-4	68.7	1.24	1.67
SE-5	76.4	2.87	3.56
SE-6	59.4	0.65	0.84

Based on the measured data it could be concluded that this method has highly reproducible tests because the RSD values were in each case below 4 % [7].

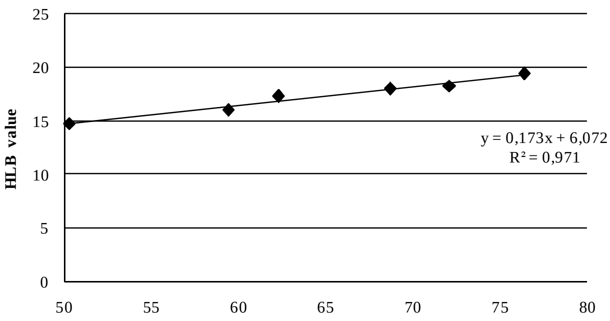

Fig. 6. The correlation between HLB value and partial solubility of surfactants

High correlation was found between HLB value and partial solubility of surfactants. This observation confirms the fact that the measured data are proportional to the solubility of the surfactants. The good correlation allows a more accurate and faster estimation of the HLB value.

4. Conclusions

In the case of developing a new method, the aqueous solutions of our own-synthesized nonionic surfactants with equal chemical type were examined, which were primarily produced for the purposes of petroleum industry. Based on our observation the applicability of an available new instrument to characterize the surfactant solubility was also studied. The presented measurement method was proved to be reliable in the comparative evaluation of water soluble surfactants effects.

It was determined that the repeatability of the transmittance values measured by the new method were reliable for the relative comparison of the solubility in water of the same type of surfactants. The defined relative standard deviation values were under the strict 5 % maximum limit.

In the given concentration range it has been observed that the growing size of the colloidal particles formed in the surfactant solution resulted in decreasing transmittance values with only a slightly decreasing tendency. Thus this method based on the absorbance of the solvents has been found appropriate to estimate also a concentration limit characteristics for the solubility of the nonionic surfactants in water.

As a consequence in the case of the analyzed fatty acid–DEA ester solutions within the applied concentration range, the fiber optic spectrophotometric analytical method was found appropriate and beneficial to compare and estimate the concentration of the turbidity limit to characterize the water solubility of this surfactants family.

Additionally, a high level of correlation was found between HLB value and partial solubility of surfactants, which facilitates a more precise determination of the HLB value.

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ДОСЛІДЖЕННЯ РОЗЧИННОСТІ ПОВЕРХНЕВО-АКТИВНИХ РЕЧОВИН У ВОДІ ЗА ДОПОМОГОЮ ВОЛОКОННО-ОПТИЧНОГО СПЕКТРОФОТОМЕТРУ

Анотація. *Показано, що емульгатори на основі олій є значним потенціалом у нафтовій промисловості. Застосування нейоногенних поверхнево-активних речовин (ПАР) при видобутку нафти набуває все більшого значення як додатку біодегредабельного типу. Розроблено прості та швидкі методи вимірювання, які можуть бути використані в промисловій практиці і придатні для контролю розчинності у воді ПАР, отриманих для вищевказаного процесу. Контроль здійснюється за допомогою волоконно-оптичного спектрофотометра AvaSpec.*

Ключові слова: *поверхнево-активна речовина, розчинність, спектрофотометр, гідрофільно-ліпофільний баланс.*