EMULSION LIQUID MEMBRANES STABILITY

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Lucrarea prezinta un studiu privind stabilitatea emulsiilor simple si a emulsiilor duble de tip apa/ulei/apa cu ajutorul microscopiei optice. Au fost studiati factorii ce influenteaza stabilitatea emulsiei: compozitia emulsiei si timpul de agitare. Pentru emulsiile duble s-a studiat comportarea emulsiei in functie de timpul de contact al emulsiei primare cu faza apoasa externa. Una dintre emulsiile obtinute a fost testata in ceea ce priveste capacitatea sa de recuperare a fenolului dintr-o solutie apoasa. Rezultatele obtinute au aratat ca studiile de stabilitate sunt necesare pentru a putea obtine cele mai bune rezultate pentru indepartarea solutilor folosind membranele emulsionate lichide.

The paper presents a study concerning emulsion stability using optical microscopy. The influence of emulsion composition, agitation time on the stability of the emulsion was studied. The influence of the contact time between the emulsion and the external phase on system stability was studied for double emulsion. One of the prepared emulsions was tested in a batch experiment for phenol removal. The obtained results sustain the idea that the stability studies are necessary in order to obtain the best results for solutes removal using emulsion liquid membranes.

Keywords: emulsion, W/O/W emulsion, stability, phenol removal

1. Introduction

Emulsions are playing an important role in variety of fields such as foodstuffs, cosmetics, pharmaceuticals, laundry and cleaning, lubricants, and so on.

Emulsions are metastable colloids made out of two immiscible fluids, one being dispersed in the other in the presence of a surface-active agent. High specific surface areas resulting from the dispersion process are not energetically favored, and therefore emulsions are thermodynamically unstable and supposed to break. The properties are high by dependent on the way they are prepared [1].

The preparation of emulsions involves many degrees of freedoms including emulsification process and conditions, the type and amount of the surfactants, the location of the surfactant, the presence of electrolytes and cosurfactants, etc. [2].

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For any emulsion system, the choice of the right emulsifier is of very crucial importance.

An important class of emulsions are the double emulsions which are complex liquid dispersion systems known also as the “emulsion of emulsion”. In practice, the double emulsion are thermodynamically unstable with a strong tendency for coalescence, flocculation and creaming. The most common double emulsions are of W/O/W emulsion [3]. Water-in-oil-in-water emulsions (W/O/W) have a growing number of applications due to their ability to entrap water-soluble materials. In most the cases double emulsion are used for slow and sustained release of active matter from an internal reservoir into the continuous phase [3]. A schematic representation of a W/O/W emulsion is presented in Fig. 1. The W/O/W emulsions can be also used to entrap matter from outer diluted continuous phase into internal phase. They can be used for water purification in this form, for advanced separation and purification of biological products especially obtained by fermentation [4-12]. The most promising application is represented by the preparation of solid or semi-solid nano-capsules [3, 13].

The formation and stability of multiple emulsions has been the object of a lot of papers [1-3, 13-16}. To ensure stability in double emulsions, it was found necessary to balance the osmotic pressure with the Laplace pressure in order to avoid Ostwald ripening [14].

A lot of measuring techniques for the study of emulsion structures are developed such as ultrasound spectroscopy, spectrophotometry, image analysis, NMR etc. [3].

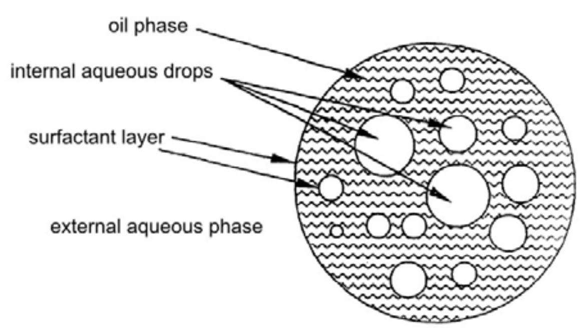

Fig. 1. The schematic representation of a w/o/w emulsion droplet.

The aim of this paper is to present an optical study concerning simple and double emulsions stability at different operating times.

2. Experimental

Chemicals: The oil materials used in this work are paraffin oil and ocatnol (from Sigma-Aldrich Co.). The surfactants used were: Span 80 (from Sigma-

Aldrich Co.) and lecithin from (from Sigma-Aldrich). The HCl and NaOH solutions were prepared in laboratory from chemical pure grade compounds supplied from Merck Co. Aliquat 336 (tricaprylylmethylammonium chloride) used as received from Fluka.

Emulsion preparation

Simple water in oil emulsion was prepared, stabilized by an oil-soluble surfactant. The emulsions were prepared by homogenizing oil and aqueous phase at high agitation speed. The next step involved the dispersion of primary emulsions into distilled water to form a double emulsion W/O/W. The ratio of W/O emulsion distilled water was 1:4.

Droplet size analysis

The droplet sizes for simple emulsions or for double emulsion were measured at different times with an optical microscope (Olympus BX 51). Simple emulsions were diluted in paraffin oil 1:1 and double emulsions were photographed without dilution.

Extraction experiment

In order to mal for the extraction experiment a volume of prepared emulsion was dispersed in a determined volume of aqueous phase with phenol, giving different phases volume ratios. Samples of the external phase were analyzed for phenol concentration using a UV-VIS spectrophotometer (Cintra 6 model -GBS Australia) at fixed wave length. Other experimental conditions are presented in Table 1.

Table 1.

Experimental conditions for phenol removal using emulsion liquid membranes

	Run 1	Run 2
Type of separation	batch	batch
Agitation speed, rpm	100	100
External phenol conc., ppm	995.7	995.7
Membrane phase	paraffin oil	paraffin oil
Surfactant conc., SPAN 80, wt%	5	5
Internal phase NaOH, conc., N	0.1	0.1
V_{em}/V_e	1/10	1/6

3. Results and discussion

Th emulsions compositions and observations on the emulsion stability are presented in Table 2. Photographs of simple W/O are double W/O/W emulsions are presented in Fig. 1. The primary emulsion consisted of paraffin oil, lecithin as surfactant and NaOH aqueous solution as internal phase.

Table2.

Emulsion compositions and stability observations

Emulsions composition	Contact time with external phase (min)	Fig. nr.	Observation (droplets diameter)
1. Membrane phase: Paraffin oil Lecithin-5% Internal phase: NaOH 0.1 N	0	1a	3-12 μm
	10	1b	5-12 μm
	20	1c	7-12 μm
	60	1d	8-21 μm
2. Membrane phase: Paraffin oil. Span 80-5% Internal phase: NaOH 0.1 N	0	2a	After 5 minutes of agitation
	0	2b	After 10 minutes of agitation
	5	2c	Stable double emulsion
	10	2d	Coalescence
3. Membrane phase: Octanol Lecithin-5% Aliquat 336-5% Internal phase: HCl 0.1 N	0	3a	Stable emulsion
	5	3b	Stable emulsion
	10	3c	Swelling

The photos are taken after 10 minutes of agitation during emulsion preparation and after 10, 20 and 60 minutes for a double emulsion W/O/W. As it can be initially, seen the emulsion is very stable (Fig. 1 a), but after long contact times with aqueous external phase (as double emulsion) diameter drops are increasing, which is a swelling consequence (Fig. 1d).

Another emulsion studied was composed of octanol as membrane phase, Span 80 as surfactant and internal phase aqueous HCl solution 0.1N.

As it can be observed in Fig. 2, the simple emulsion W/O is stable during preparation (after 5 and 10 minutes of agitation). But when it is contacted with an aqueous phase and becomes a double emulsion (W/O/W) we can observe some changes after 5 and 10 minutes of contact times. The drops begin to swell and even to coalesce, although the emulsion doesn’t brake (Fig. 2c and d).

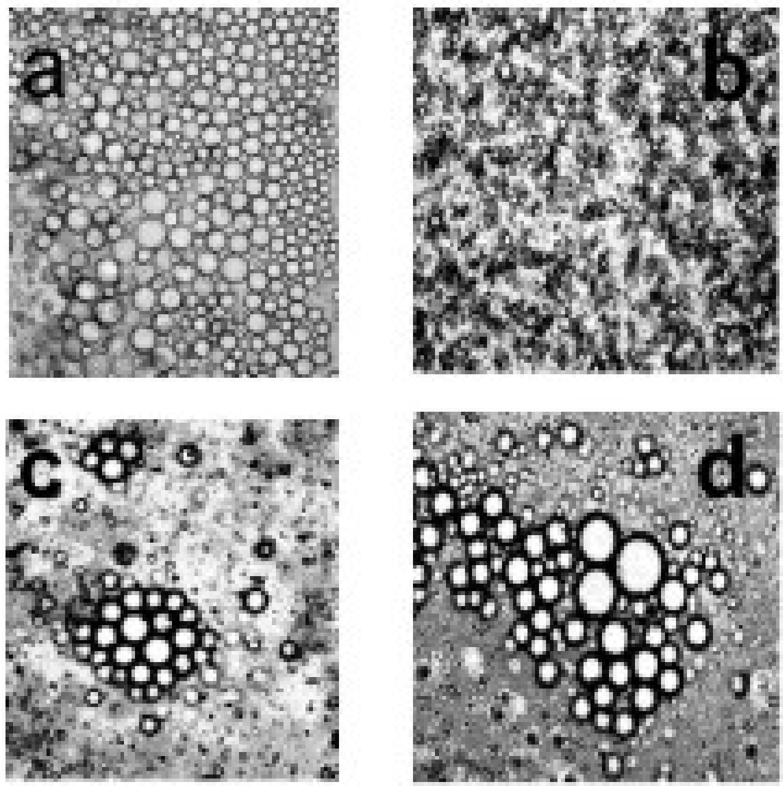

Fig. 1. Photographs of the emulsion 1 a) Emulsion during preparation (after 10 minutes of agitation);
b) After 10 minutes of contact with aqueous external phase; c) After 20 minutes of contact with aqueous external phase; d) After 60 minutes of contact with aqueous external phase, (magnification rate X500).

The last emulsion studied was composed of octanol as membrane phase, lecithin as surfactant, aliquat 336-5% as extractant and aqueous HCl solution 0.1N as internal phase. The photographs of this emulsion are presented in Fig. 3.

As it can be observed, the emulsion is initially stable (Fig. 3a), but the stability of the emulsion is changing during the contact time with aqueous external solution. We can observe drop diameter the increasing which is produced by the emulsion swelling (Fig. 3b and 3d). Even the emulsion doesn't break; the emulsion swelling is not desirable, especially when such double emulsion is used for water purification.

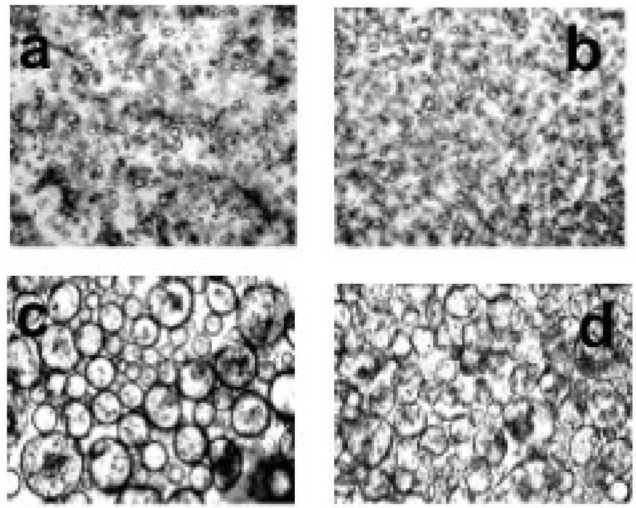

Fig. 2. Photographs of the emulsion 2 a) after 5 minutes of agitation during preparation, b) after 10 minutes of agitation during preparation 3) after 5 minutes of contact with aqueous external phase; d)Emulsion after 10 minutes of contact with aqueous external phase (X200).

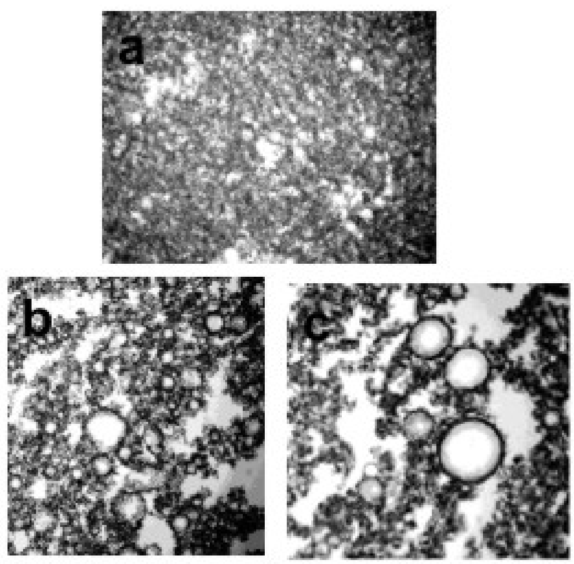

Fig. 3. Photographs of the emulsion 3 a) After 10 minutes of agitation during preparation, b) After 5 minutes of contact with aqueous external phase; c) After 10 minutes of contact with aqueous external phase; (X200).

The first emulsion from Table 2 was tested in a batch experiment for phenol removal from an aqueous solution. The initial concentration of phenol was 995.7 ppm. The parameter which was varied was the treating ratio (Ve/Vex, where Ve is the emulsion volume and Vex is the volume of the external phase). The experimental results obtained are presented in Fig. 5.

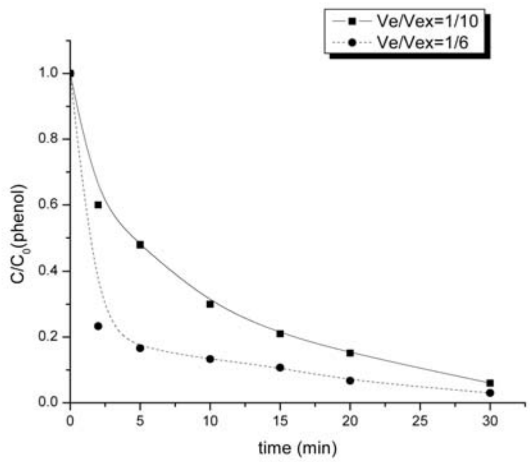

Fig. 5. Experimental phenol dimensionless concentration in external phase vs the time for different treating ratios.

The removal efficiency was calculated and is greater for a treating ratio Ve/Vex=1/6 as it was expected, beacuse the volume of emulsion is increasing in the unit volume of the external phase, and the mass transfer area is consequently increasing. Also the experimental curves depicted in Fig. 5 demonstrate that the emulsion used is stable during operation, because we have obtained a continuous decreasing of phenol concentration. In the case of emulsion lackage one can observe an icreasing of solute concentration.

Conclusions

The experimental study shows that optical microscopy can be used to study the stability of simple and double emulsions. Emulsion swelling can be also observed. From the studied emulsions we can conclude that primary emulsions are stable after preparation even they contain Span 80 or lecithin as surfactants, but when they are used to obtain a double emulsion, the stability is decreasing in time and a process of swelling begin.

One of the stable emulsion was tested in a typical experiment for phenol removal using emulsion liquid membranes. The results obtained confirmed that the stability of the emulsion was maintained during the operating time.

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