

# Emulsion Membranes Iodine Separation

## I. Preparation of organic phase membrane emulsion / receiving aqueous solution

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*One of the major obstacles in membranes achievement is represented by the difficulty of determining the emulsion stability domain, in correlation with flow regime. The main parameters which are taken into account in this case are: feed solution droplet size, the density of the two phases, organic and respectively, aqueous, the nature of surfactants and working temperature. In this paper are established the conditions for obtaining the receiving aqueous solution/organic solvent primary emulsions (RP / M) necessary in the separation of iodine from poor sources. Basically, the aqueous receiving phase is dispersed, in the presence of a surfactant in the organic phase which constitutes the membrane. In order to obtain emulsions of water in the organic phase, the aqueous receiving phase is dispersed under vigorous stirring in the organic phase. The emulsions stability was monitored over time, depending on the: pH of the receiving phase, aqueous/organic phase volumetric ratio, nature and concentration of the surfactant. The time at which the occurrence of single-phase system first layer is observed represents the emulsion life time.*

*Keywords: iodine separation, emulsion membranes, emulsion stability, recuperative separation*

Since the 60's – 70's, an innovative separation technique has been proposed: the double emulsions method or emulsion liquid membrane (ELM) [1-4]. The name indicates that the system with three liquid phases: a source aqueous phase (SP), the membrane organic phase (M) and a receiving aqueous phase (RP) is stabilized by an emulsifying agent in a concentration of 1-5%, according to liquid membrane [5-7]. In a first step, the receiving phase, which typically has a much smaller volume than the source phase, is dispersed by a vigorous stirring in an intermediary organic phase [8,9].

The primary emulsion obtained is consistent and stable due to the microscopic size of the receiving phase droplets (0.1-10  $\mu\text{m}$ ) and due to high content of specific emulsifier [10,11].

The DEM system (fig. 1) is created, in the next step, when the source phase is mixed with the emulsion. For this purpose, the primary emulsion is dispersed in the source phase under gentle stirring [12,13]. The emulsions used for the separation of inorganic compounds from various aqueous systems are composed of organic solvent based membrane in which a phase carrier and a specific receiving phase are present. [14-17].

In the receiving phase of the double emulsion membrane system is required the presence of a reactant capable of converting the dissolved chemical species into a waterproof form through membrane. Waterproof species are caught within the primary emulsion and therefore, the chemical equilibrium is shifted in the meaning of chemical species permeation towards the receiving phase, maintaining the process driving force, which is the concentration gradient [17,18].

The formation of receiving aqueous phase/organic solvent emulsions involves:

- choice of receiving aqueous phase;
- selecting an organic solvent with a very low solubility in the aqueous phase;
- determination of the nature and concentration of the emulsion stabilizing agent (emulsifier);
- determining the mechanical stirring conditions.

After selecting the organic solvent - receiving phase pair, will follow the determination of emulsifier nature and concentration.

When the emulsifiers are chosen the size HLB (hydrophilic-lipophilic balance) is used, which implies low levels in order to stabilize the emulsions [19].

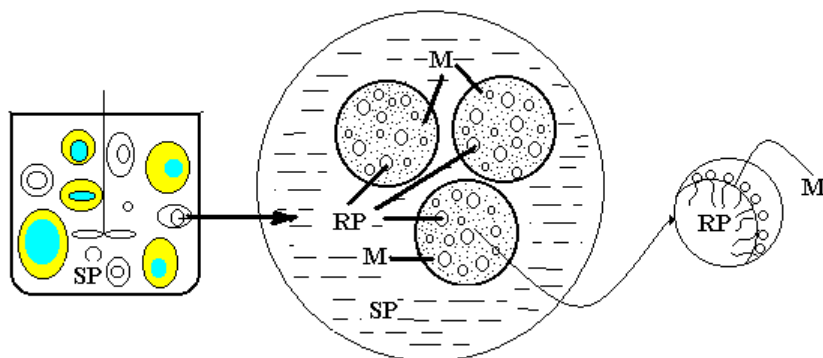


Fig. 1. Double emulsion system: receiving phase/organic solvent (RP/M) dispersed in source phase (SP)

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The choice of liquid membrane components in the emulsion liquid membrane system is very important for the selectivity, efficiency and stability of the emulsion.

Factors such as: the membrane solvent, the concentration of the emulsifier and the droplet size are crucial for: the membrane stability, a perfect separation and an efficient extraction capacity of the emulsion liquid membrane systems [20].

Receiving phase parameters such as: its volumetric fraction, pH or volumetric ratio between the membrane phase and the receiving phase influences the functioning of the ELM system [21].

In this technique, small volumes of emulsion are used for efficient treatment of large volumes of aqueous solution. The dissolved species which can be removed through this process are: organic and inorganic, neutral, ionic, acidic or basic compounds [17-23].

After components separation, occurs the emulsion breaking through physico-mechanical (thermal, electrical, ultrafiltration, flow regime change) or chemical (adding chemical agents) methods [24-26].

One of the major obstacles in membranes achievement is represented by the difficulty of determining the emulsion stability domain, in correlation with flow regime. The main parameters which are taken into account in this case are: feed solution droplet size, the density of the two phases, organic and respectively, aqueous, the nature of surfactants and working temperature.

Achieving an effective separation depends on: the relative solubility of the species which are transferred to the considered phase, the chemical potential gradient (most commonly the difference in concentration), pH, redox potential, complexation, the nature of the carrier (carrying capacity, carrier loss, transport accessibility) and receiving phase quantity relative to source phase.

Injudicious choice of the ratio between the two phases reduces the advantage of large surfaces in contact, given by emulsion membranes, leading to a simple extraction [18-21].

Making technically applicable emulsion membranes requires getting an extremely stable primary emulsion which contains the receiving phase.

Basically, the aqueous receiving phase is dispersed, in the presence of a surfactant in the organic phase which constitutes the membrane.

In order to obtain emulsions of water in the organic phase, the aqueous receiving phase is dispersed under vigorous stirring in the organic phase.

The emulsions stability was monitored over time, depending on the: pH of the receiving phase, aqueous/organic phase volumetric ratio, nature and concentration of the surfactant.

The time at which the occurrence of single-phase system first layer is observed represents the emulsion life time.

In this paper are established the conditions for obtaining the receiving aqueous solution/organic solvent primary emulsions (RP / M) necessary in the separation of iodine from poor sources.

## Experimental part

### Materials and equipment

As organic solvents were used hydrocarbons: benzene, toluene, xylene, kerosene provided by Merck and three types of alcohols also provided by Merck (medium normal aliphatic alcohols C6, C8 and C10) and a domestic production technical alcohol (cyclohexanol).

Merck provided alcohols have refractive index at 20°C in the range 1,4100 and 1,4300, and the flash point between 63 and 108°C.

The emulsifiers used in reverse emulsion formation were: technical nonyl phenol (NF4) DDSNa sodium dodecyl sulphate (Merck), Span 80 (Fluka), Span 20 (Fluka) and ionic surfactants: pyridinium salts (Merck), Hyamine (Merck) and sodium dodecylbenzenesulfonate (synthesis product).

In order to obtain RP/M type primary emulsions and RP / M / SP type double emulsions was used Heidolph RZR 2041 stirrer with the following characteristics: maximum allowed viscosity of 100,000 mPa s; two-speed stages: stage I 40 - 400rpm, stage II 200 - 2000rpm, engine power 37W; shaking force 520 Ncm; digital display.

In order to determine the influence of carrier concentration and emulsifier content on the emulsions stability was used TurbiscanLab Plus device having the following technical characteristics: particle size measurement range: 0.05 ÷ 1000µm; particle concentration: up to 95% for emulsions; measuring technique: multiple scanning, temperature range: from 5°C above ambient temperature up to 60°C, accuracy ± 0.5 ° C; sample requirements: 22 mL maximum volume, samples must be inert in contact with glass or Teflon; cells samples: glass cells flat-bottomed provided with modified polycarbonate cover and butyl/Teflon sealing ring; Windows 95, 98, 2000 compatible software (recommended) and NT Port: RS 232 C or USB.

Determination of iodine concentration in emulsion membrane system phases was carried out with a CAMSPEC spectrometer with the following characteristics: local control software - includes all methods, basic mode - absorbance measurements, % T and concentration; quantitative - can be used down to 10 standard solutions for one calibration; wavelength scanning - 200-800 nm; multiple wavelengths - up to 10 wavelengths, performance validating - for GLP according to laboratory.

Motic microscope equipped with video camera was used to establish the life time of the primary emulsion (RP / M) and has the following performances: binocular/trinocular microscope with 30° tilting angle, rotatable at 360° that provides comfort to the operator, WF PL10x/20mm with dioptric compensation on both tubes and adjustment of interpupillary distance; iris diaphragm and continuous control intensity for resolution and contrast control provides homogeneous and fair illumination for all magnitudes; micrometer screw for fine adjustments with coaxial focus; rapid movement stroke 25 mm; fine division value 2 micrometers; work surface (140 x 135mm) can move XY direction (76x50 mm); metal surface covered by an epoxy layer stand; power supply: 110-220 V.

## Results and discussions

In the present stage of separation methods development, emulsion membrane separation share has not reached the desired level because of the two major problems which involve their application: obtaining stable primary emulsions (at least 60 min) and the difficulty of breaking the primary emulsions (after the operation) [20-26].

### Setting basic parameters in obtaining receiving phase/organic solvent emulsions

The first step in developing emulsion membrane techniques is the achievement of stable primary emulsions but, in experimental research aiming inorganic compounds

Solvent	Surfactant concentration			
	SPAN 20	SPAN 80	NF4	DDSNa
benzene	1-5%	1-3%	1-5%	1-3%
toluene	1-5%	1-3%	1-5%	1-3%
xilene	1-5%	1-3%	1-5%	1-3%
kerosene	1-5%	1-3%	1-5%	1-3%

**Table 1**  
TYPES OF SOLVENTS AND SURFACTANTS USED IN THE EXPERIMENTS

separation, such as iodine, with emulsion membranes, is still to elucidate other related issues, but not unimportant, such as: swelling the emulsion, the emulsion adhesion to the pertractor walls; emulsion stabilizing agents recovery, kinetic and hydrodynamic separation process.

Making technically applicable emulsion membranes impose obtaining a remarkably stable primary emulsion containing receiving phase.

The emulsion stability was monitored over time, depending on the receiving phase pH, organic phase/ aqueous phase volumetric ratio, surfactant nature and concentration.

The time at which the occurrence of single-phase system first layer is observed represents the emulsion life time.

#### *The influence of nature and concentration of non-ionic surfactants*

In 100 mL of organic solvent (benzene, toluene, xylene, kerosene) was dissolved an amount from a certain surfactant (NF4, SPAN 20, SPAN 80, DDSNa sodium dodecyl sulfate) (table 1).

The concentrations of surfactant in organic solvent solutions were between 1-5%, or 1-3%, depending on its solubility.

Each solution was mixed, in measuring cylinders provided with glass stopper under vigorous stirring with different volume of distilled water.

The ratio between the volume of surfactant and distilled water solution ranged from 0.5 to 4.5. Stirring time was 30 min, the same for all samples.

The separation phenomenon (the appearance of monophasic layer) was visually monitored (with digital video camera), and the time was measured with a stopwatch.

Nonionic surfactants (SPAN 20 and SPAN 80) have a higher stabilizing effect than ionic surfactants which results in phase separation time, which reaches several tens of minutes.

The influence of DDSa and nonyl ethoxylated phenol NF<sub>4</sub> is similar, thus, increasing the concentration increases the lifetime of the emulsion and the maximum effect is experienced in terms of phases ratio close to unity (fig. 2).

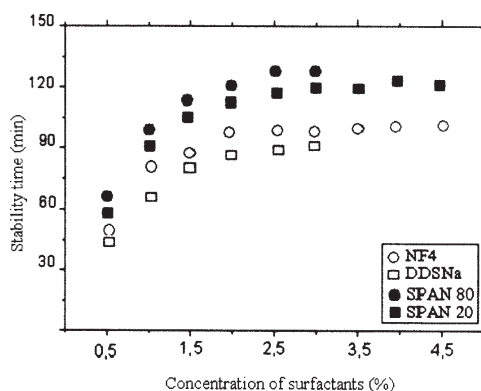


Fig. 2. Toluene / water emulsion stability depending on the surfactant concentration at volume ratio 1:1

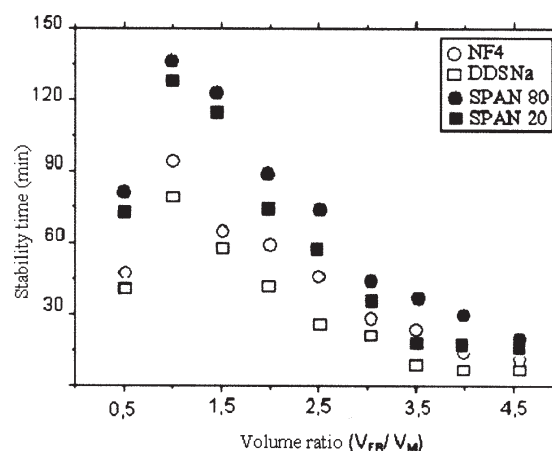


Fig. 3. Toluene/water emulsion stability depending upon the phases volume ratio for various surfactants, at 2% concentration

The optimal surfactant concentration is 1.5 -2.5% (fig. 2), but in subsequent experiments can reach 3% because at the contact with the source phase and at high receiving phase/membrane volume ratio, the losses become important.

#### *The influence of membrane phase/receiving phase concerning primary emulsion stability*

Emulsion membrane separations are technologically approved because the solvent necessary amount has a volume less than or equal to the receiving phase and 10 to 100 times lower than the source phase [18, 21, 22-25]. From the desire of reducing organic solvent volume / receiving phase volume ratio can be reached primary emulsion destabilization and therefore this ratio must be known or determined.

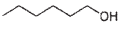



Increasing the life time of the emulsion is non-linear (fig. 3) presenting both a maximum around the unit ratio and a minimum which is hard to explain at 1:4.5 phases ratio.

Once the phases ratio reaches value 1, the stability decrease is dramatic, and may be considered that at value 1.5 it is inappropriate to discuss of primary emulsion usable in emulsion membranes technique (fig. 3).

From the experiments carried out with nonionic substances on the toluene/aqueous solution system results that 1:1 ratio usage is favorable regardless of the surfactant nature and concentration.

Similar effects were observed also at toluene/water emulsion stability tests in the presence of surfactant SPAN 80. In figure 3 is firstly observed that stability achieves few days, being higher in the case of unit ratio between phases. At 1:4 ratio minimum stability does not appear, but after reaching 1, the emulsion practically won't form, regardless the surfactant concentration used.

It can be said that at a ratio 1:1 solvent: water, the use of SPAN 80 as emulsion stabilizer will provide a sufficient life time for primary emulsion in order to use it in a membrane system.

Characteristic	<i>n</i> -C <sub>6</sub>	<i>n</i> -C <sub>8</sub>	<i>n</i> -C <sub>10</sub>	<i>c</i> -C <sub>6</sub>
				
Refractive index (n <sub>D</sub> <sup>20</sup> )	1.4178 (20°C)	1.428-1.431	1,434-1,445	1,4656
Density (d <sub>4</sub> <sup>20</sup> ) g/cm <sup>3</sup>	0.8136 g/cm <sup>3</sup> (20°C)	0.8240 g/cm <sup>3</sup>	0.8297 g/cm <sup>3</sup>	0.962 g/cm <sup>3</sup>
Water solubility (20°C) g/L	0.59 g/100 ml (20°C)	0.3 g/L (20°C)	12 ppm sau 0.0037g/l 25°C	3.60g/100mL (20 °C)
Boiling point °C	158°C	195 °C	232.9°C	161°C
Melting point °C	-46.7°C	-16 °C	6.4°C	25°C
Molar mass (g/mol)	102.17 g/mol	130.23 g/mol	158.28 g/mol	100.16 g/mol
Flash point °C	63°C	81°C	108°C	68°C
Self-ignition point °C	290°C	270 °C	255°C	300°C
Explosive limit	0.3-1.2 % vol	0.8% vol	-	2-11.2% vol

**Tabele 2**  
CHARACTERISTICS OF MEMBRANE  
SOLVENTS USED

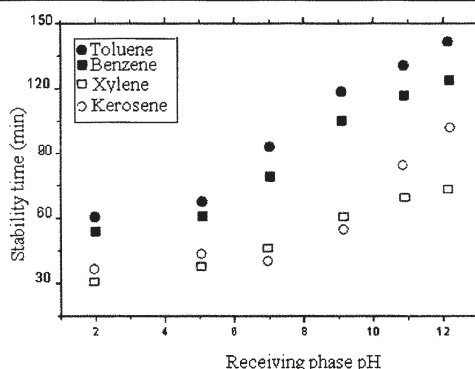


Fig. 4. Stability of the emulsion according to the pH of the receiving aqueous solutions, in the case of four kinds of solvent

#### The influence of receiving phase pH on the primary emulsion stability

The experiments regarding the effect of receiving aqueous phase pH on the stability of organic solvent/water emulsion were carried out using organic solvents: benzene, toluene, xylene and kerosene realizing an emulsion with organic solvent and Span 80, in which the concentration of surfactant is 2% and water. We worked with equal volumes of aqueous phase and organic phase (solvent - SPAN 80), aiming to establish the time after which the phases begin to separate.

From figure 4 it is seen that the stability of the emulsions increases with increase in pH of the receiving phase for the three types of hydrocarbons. It is also noted the increased stability of emulsions using toluene as solvent.

Following these experiments it appears that in general, emulsion membranes with hydrocarbon membrane phase can be used especially to separate acidic chemical species involving an aqueous receiving phase with alkaline pH favourable for the emulsion stability.

The emulsions stability was monitored over time according to solvent type, the pH of the receiving phase, the volume ratio between aqueous phase - organic phase, the nature and concentration of the surfactant.

The experiments were carried out using three organic solvents: toluene, benzene and xylene.

Regardless of the operating conditions, the use of the toluene resulted in obtaining the greatest stability of the emulsions.

The nonionic surfactants (NF4, SPAN 20, SPAN 80) have a higher stabilizing effect than the ionic surfactants

(DDSNa) which results in time stability, which reaches several tens of minutes.

The optimal working concentration for all surfactants tested it was at the upper limit of concentration, which generally does not exceed 2.5%.

From the experiments done with nonionic substances in the system toluene/aqueous solution results that using a 1:1 volume ratio corresponds to a maximum of stability for each of the surfactants used. The stability of the prepared emulsions increases with increasing the pH of the aqueous solution which is the basis to obtain them.

It can be said that in the case of a 1:1 solvent-water ratio, using SPAN 80 as emulsion stabilizer at a concentration of 2.5% ensures a life time of the primary emulsion enough (at least 1.5 h) for using it in a membrane system, in the full pH range.

#### Water /alcohol emulsion membranes preparation

Achieving an effective separation depends on: the relative solubility of the species which are transferred to the considered phase, the chemical potential gradient (most commonly the difference in concentration), pH, redox potential, complexation, the nature of the carrier (carrying capacity, the carrier loss, transport accessibility) and the amount of receiving phase relative to source phase.

Injudicious choice of the membrane organic phase or the ratio between the two phases reduces the advantage of large surfaces in contact, given by emulsion membranes, leading to a simple extraction [26-28].

For the study of iodine separation from dilute aqueous solutions was chosen a membrane based on normal medium aliphatic alcohols C<sub>6</sub>, C<sub>8</sub> and C<sub>10</sub> and cyclohexanol, given several factors, such as: relatively low solubility in water, chemical inertness, lack of toxicity, relatively low flammability, biodegradability, low cost and the fact that are currently used in conventional processes of separation by solvent extraction (table 2).

#### The influence of nature and concentration of the surfactants

In a measuring cylinder provided with ground glass stopper were inserted *a* mL of the organic solvent (*n* hexanol, *n* octanol, *n* decanol and cyclohexanol) in which has been dissolved an amount of a particular surfactant (SPAN 20, SPAN 80, dodecyl pyridinium chloride - CDDPy, tetradecyl pyridinium chloride - CTDPy, octadecyl pyridinium chloride - CODPy, dodecyl benzene sodium

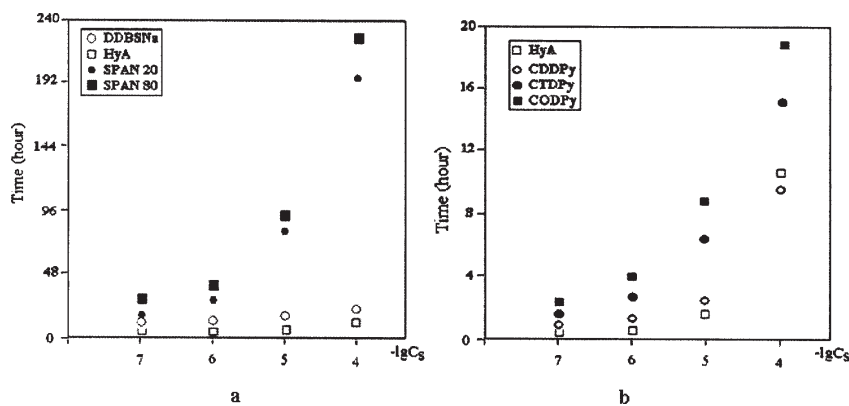


Fig. 5. Stability of alcohol/surfactant aqueous solution emulsion: ionic and non-ionic surfactants (a) and cationic surfactants (b)

sulphonate - DDBSNa and Hyamina - HYA) and (100-a) mL of distilled water. The surfactant solutions in organic solvent had concentrations between  $10^{-7}$  and  $10^{-4}$  M.

Each alcohol solution was emulsified in graduated cylinders fitted with ground glass stopper, under vigorously stirring with different volumes of distilled water.

The volume ratio between the volume of surfactant and distilled water solutions ranged from 0.1 to 2. The stirring time was 20 minutes the same for all samples.

The separation phenomenon, coalescence or emulsion breakage (the appearance of mono phase layer) was followed optically (Motic microscope), and the time was measured with a stopwatch.

Initial determinations aimed, using the normal octyl alcohol and unit ratio between the organic and aqueous phases ( $V_o / V_w$ ), to establish the influence of surfactant nature and concentration.

The experiments (fig. 5 a and b) that were done reveal that the increase of surfactant concentration increases life (stability) of the emulsion, but the nonionic surfactants (SPAN 20, SPAN 80) have a higher stabilizing effect by approximately an order of magnitude, compared to ionic surfactants, which results in a phase separation time, which reaches several tens of hours.

The influence of the cationic surfactants is similar as allure (fig. 5 b), thus, increasing the concentration increases lifetime of the emulsion and the maximum stabilizing effect is given by the surfactant with higher hydrocarbon chain.

Thus, the stabilizing effect of the pyridinium salts increases in the order: Hyamine < dodecyl pyridinium chloride - CDDPy < tetradecyl pyridinium chloride - CTDPy < octadecyl pyridinium chloride - CODPy.

The anionic surfactant used has a stabilizing effect comparable to that of the cationic surfactants, with the same chain (DDBSa-COPy).

The stability of the *n* octanol/ surfactant solution in distilled water emulsions depends in a large extent on the concentration and nature of the surfactant.

Thus, if the breakage of the emulsion in the presence of SPAN type surfactants occurs at 1 day, for a concentration of  $10^{-7}$  M, at 8-10 days, for a concentration of  $10^{-4}$  M, in the

case of ionic surfactants (Hyamina and dodecylbenzenesulfonate), emulsions breaking occurs after a few hours.

It is important to note that the non-ionic surfactant is higher than the ionic surfactant, and in the case of cationic surfactants (alkyl pyridinium chloride) the increase of hydrocarbon chain contributes to increasing the stability of the emulsion, which is evident at relatively large concentrations of ( $10^{-4}$  M).

#### The influence of receiving phase/membrane phase ratio on primary emulsion stability

Emulsion membrane separations are agreed because the solvent necessary amount has a volume less than or equal to the receiving phase and 10 to 100 times lower than the source phase.

From the desire of reducing the ratio between the organic solvent volume and receiving phase volume can be reached primary emulsion destabilization and therefore this ratio must be known or determined.

Using similar surfactant concentrations,  $10^{-4}$  M, at neutral pH of the aqueous phase, but at different volume ratios ( $V_o/V_w$ ) it was found that regardless of the surfactant nature, the most stable emulsions are at volume ratios ( $V_o / V_w$ ), equal to 1 (fig. 6-8).

As expected, after the experiments presented in the previous paragraph, the stability of emulsions in the presence of non-ionic surfactants (SPAN type) is much higher than that of the emulsions based on ionic surfactants, regardless of the alcohol used as organic phase.

However, it can be shown that there are noticeable differences in the stability of the emulsions based on *n* alkyl alcohols and cyclohexanol.

Thereby, for the non-ionic surfactants (fig. 6 a and b) at  $V_o/V_w$  subunit ratios the emulsions of alcohols with higher hydrocarbon chain are more stable, while the emulsions obtained at  $V_o / V_w$  ratios unit and above unit are more stable for short hydrocarbon chains.

The stability of emulsions using SPAN 80 and SPAN 20 is superior throughout the volume ratios range studied (0.25

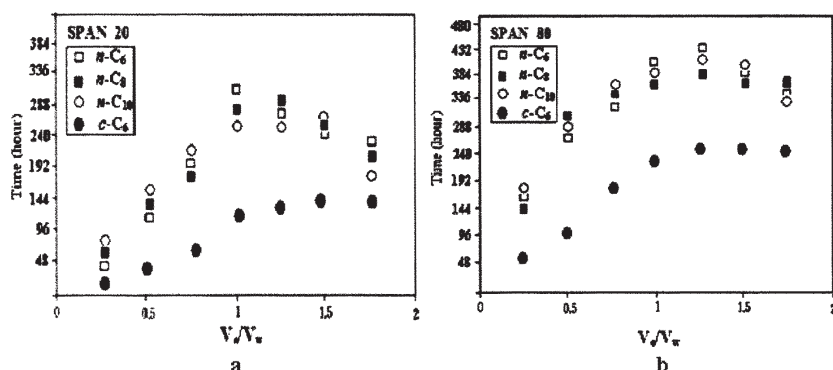


Fig. 6. Stability of alcohol (*n*-C<sub>6</sub>, *n*-C<sub>8</sub>, *n*-C<sub>10</sub>, *c*-C<sub>6</sub>) aqueous solution of SPAN 20 (a) and SPAN 80 (b) emulsions

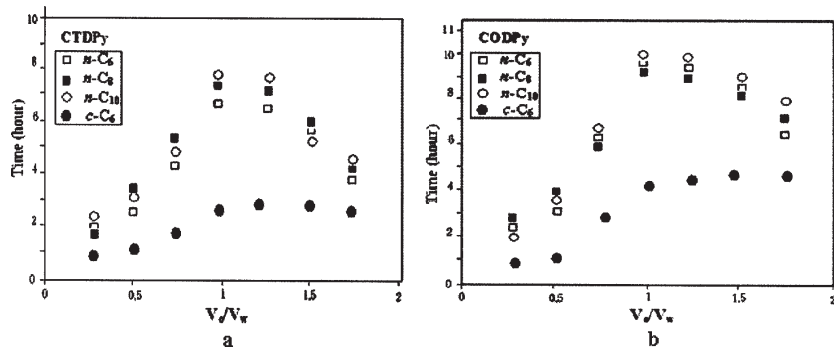


Figure 7. The stability of emulsions based on alcohol ( $n-C_6$ ,  $n-C_8$ ,  $n-C_{10}$ ,  $c-C_6$ )/cationic surfactant aqueous solution: tetradecyl pyridinium chloride -CTDPy (a) and octadecyl pyridinium chloride -CODPy (b)

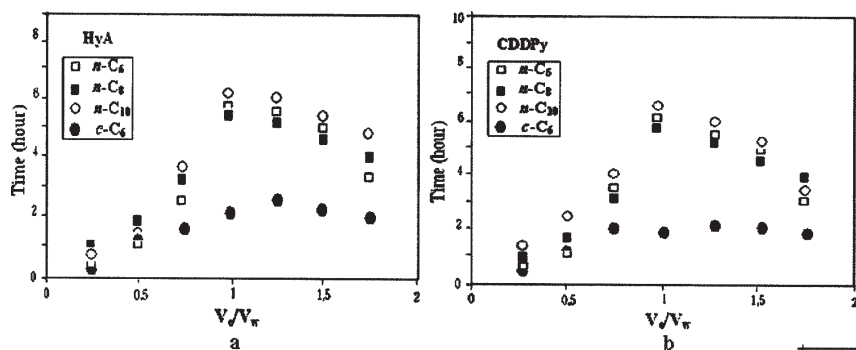


Fig. 8. The stability of emulsions based on alcohol ( $n-C_6$ ,  $n-C_8$ ,  $n-C_{10}$ ,  $c-C_6$ )/cationic surfactant aqueous solution: Hexadecyl trimethyl ammonium chloride- HyA (a) and Dodecyl pyridinium chloride-CODPy (b)

to 1.75), and breaking the emulsion after several days allows the use of both surfactants for preparation and usage as emulsion membranes.

Ionic surfactants have a very similar behaviour, however, the stability of the emulsions obtained is a few hours up to 10 h (fig. 7b).

Long-chain cationic surfactants (CODPy), give superior stability to the short-chain hydrocarbon ones (CDDPy).

Although observable, even in this case, differences of stability depending on the: nature of alcohol, chain length, from  $n$  hexanol to  $n$  decanol are not relevant and we are able to conclude that essential is the  $V_o/V_w$  ratio (fig. 6-9).

In the case of anionic surfactant is recommended to avoid the deviation from unit ratio,  $V_o/V_w$ , especially for  $n$  hexanol, thereupon the stability becomes so small that there may be concern not to use the emulsion for separation experiments.

In the case of ionic surfactants the emulsion breakage occurs after a few hours and therefore it is very important to have a volume ratio close to unity in order to use such systems as emulsion membrane.

Increasing the life time of the emulsion is non-linear (fig. 6-9) presenting both a maximum around the unit ratio and a minimum which is hard to explain at 1:4 phases ratio.

Once the phases ratio reaches value 1, the stability decrease is dramatic, and may be considered that at value 1.5 it is inappropriate to discuss of primary emulsion usable in emulsion membranes technique (fig. 9).

From the experiments carried out with ionic substances on the alcohol/aqueous solution system results that 1:1 ratio usage is favorable regardless of the surfactant nature and concentration.

Similar effects were observed also in the tests of alcohol / water emulsion stability in the presence of SPAN 20 and SPAN 80 surfactants.

Firstly, in figures 6-9 it is observed that the stability reaches few days, being higher at unit ratio between phases.

It can be seen that at a 1:1 ratio between solvent and water, the use of SPAN as emulsion stabilizer provides a long enough life time for the primary emulsion in order to

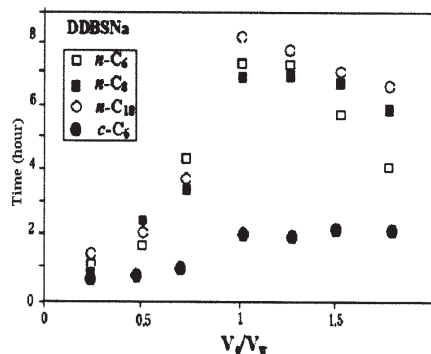


Fig. 9. Stability of emulsions based on alcohol ( $n-C_6$ ,  $n-C_8$ ,  $n-C_{10}$ ,  $c-C_6$ )/anionic surfactant aqueous solution: sodium dodecylbenzenesulfonate - DDBSNa

be used in a membrane system, even at the technological level.

#### Receiving phase pH influence on primary emulsion stability

The experiments regarding the effect of receiving aqueous phase pH on the stability of the emulsion based on organic solvent / water were carried out using as organic solvents normal aliphatic alcohols:  $C_6$ ,  $C_8$  and  $C_{10}$ , realizing an emulsion with an organic solvent and a surfactant, wherein the surfactant concentration is  $10^{-4}$  M and water.

We worked with equal volumes of aqueous and organic phase (solvent - surfactant), aiming to establish the time after which the phases begin to separate. The pH value was adjusted with hydrochloric acid and sodium hydroxide, the accuracy falling within the indicated value of  $\pm 3\%$ .

From figures 10 and 11 it is seen that the stability of the emulsion increases with increase in pH of the receiving phase for the three kinds of alcohols and the four kinds of ionic and non-ionic surfactants. It is also noted the increased stability of the emulsions which are using SPAN as surfactant.

The values for lifetime are within the limits previously observed, both for ionic (some hours) and nonionic (some days) surfactants.

The stability of emulsions based on ionic surfactants in hexyl alcohol is, in general, significantly less than that of the emulsions based on  $n$  octanol and  $n$  decanol, in the range of pH 8-12 (fig 10).

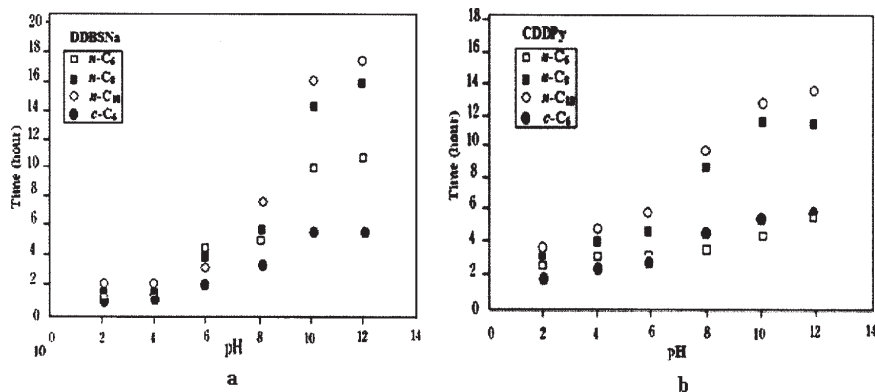


Fig. 10. Stability of emulsions based on alcohol ( $n\text{-C}_6$ ,  $n\text{-C}_8$ ,  $n\text{-C}_{10}$ ,  $c\text{-C}_6$ ) / ionic surfactant aqueous solution according to receiving aqueous solution pH

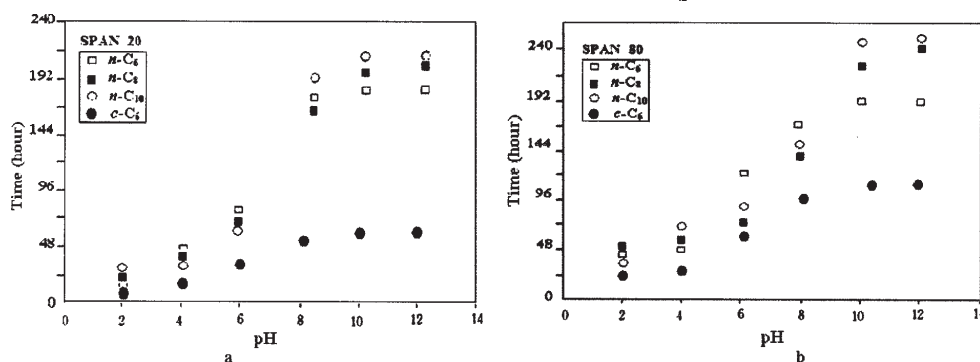


Fig. 11. Stability of emulsions based on alcohol ( $n\text{-C}_6$ ,  $n\text{-C}_8$ ,  $n\text{-C}_{10}$ ,  $c\text{-C}_6$ ) / nonionic surfactant aqueous solution according to receiving aqueous solution pH

The stability of the emulsions based on non-ionic surfactants in hexyl alcohol is similar or comparable with the one of the emulsions based on  $n$  octanol and decanol, throughout the range of pH (fig. 7).

After these experiments it appears that in general, the emulsion membranes having as membrane phase a medium aliphatic alcohol can be used especially to separate acidic compounds which involves an alkaline pH of the receiving aqueous phase favorable to the emulsion stability.

The emulsions stability was monitored over time according to the: solvent type, pH of the receiving phase, the volume ratio between aqueous phase and organic phase, nature and concentration of the surfactant.

The experiments were carried out using four organic solvents: normal aliphatic alcohols  $C_6$ ,  $C_8$ ,  $C_{10}$ , and cyclohexanol. Whatever the working conditions, octanol and decanol allowed obtaining the highest emulsions stability compared with cyclohexanol, who allowed obtaining the smallest stability.

The nonionic surfactants (SPAN 20 and SPAN 80) have a higher stabilizing effect compared to ionic ones materialized in a stability time, which reaches from 1-2 hours to tens of hours (a few days).

## Conclusions

The emulsions used for iodine separation was monitored, depending on the: solvent type, pH of the receiving phase, the volume ratio between aqueous phase and organic phase, the nature and concentration of the surfactant for hydrocarbon type solvents.

Regardless of the operating conditions, the toluene allowed to obtain the emulsions with the greatest stability.

The optimal working concentration for all surfactants tested it was at the upper limit of concentration, which generally does not exceed 2.5%.

From the experiments done with nonionic substances in the system toluene/aqueous solution results that using a 1:1 volume ratio corresponds to a maximum of stability for each of the surfactants used.

The stability of the prepared emulsions increases with increasing the pH of the aqueous solution which is the basis to obtain them.

It can be said that in the case of a 1:1 solvent-water ratio, using SPAN 80 as emulsion stabilizer at a concentration of 2.5% ensures a life time of the primary emulsion enough (at least 1,5 h) for using it in a membrane system, in the full pH range.

The experiments were carried out using four organic solvents: normal aliphatic alcohols  $C_6$ ,  $C_8$ ,  $C_{10}$ , and cyclohexanol. Whatever the working conditions, octanol and decanol allowed obtaining the highest emulsions stability compared with cyclohexanol, which allowed obtaining the smallest stability.

From the experiments carried out with ionic substances on the alcohol/aqueous solution system results that 1:1 ratio usage is favorable regardless of the surfactant nature and concentration.

Similar effects were observed also in the tests of alcohol/water emulsion stability in the presence of SPAN 20 and SPAN 80 surfactants, showing that the stability reaches few days, being higher at unit ratio between phases.

Thereby, for the non-ionic surfactants at  $V_o/V_w$  subunit ratios the emulsions of alcohols with higher hydrocarbon chain are more stable, while the emulsions obtained at  $V_o/V_w$  ratios unit and above unit are more stable for short hydrocarbon chains.

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