A COMPARATIVE STUDY ON THE SYNTHESIS OF ROSE OIL CONTAINING MICROCAPSULES BY COMPLEX COACERVATION USING DIFFERENT SOLVENTS

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ABSTRACT

Microencapsulation of various substances encompasses a vast field of exceptional application in modern medicine, pharmacy, perfumery and cosmetics, biomedical engineering, as well as in the textile, petroleum and general industries. Although this process can be effected in different ways, depending on its nature (physical, chemical or physicochemical process), physicochemical group of procedures and in particular coacervation is one of the most preferred in terms of ecological purity and biodegradability of the materials used in this method of producing microcapsules. The material in coacervation process used to produce the microcapsules is entirely from natural sources, which would allow their biodegradability over time. The coacervation can be divided into two types: simple and complex. In the microencapsulation of expensive natural products, they need to be diluted with a suitable solvent for three reasons: on the one hand - due to the cost of the encapsulated substance, on the second - to stabilize the core material, and on the third hand - to increase the efficiency of the process, resulting in higher yield and quality of the microcapsules obtained.

This article examines the effect of the type of solvent (playing the role of media for diluting the encapsulated substance) on the encapsulation efficiency, yield, and quality of the microcapsules obtained, in the microencapsulation of rose oil using the complex coacervation process.

Keywords: microencapsulation, biopolymers, natural compounds, fragrances, oils, gelatin, rose oil, complex coacervation, solvents, renewable materials.

INTRODUCTION

In the current state of nanotechnology, the production of capsules with small size and long-lasting effect is one of the modern directions in chemistry, which in turn has a long history [1 - 11]. In practice, this process allows the wrapping of extremely small quantities of different products bearing the common name core material, surrounded by a shell made of the concrete material. The main purpose of this process is to protect the active core material from the external environment and, on the other hand, to allow a longer duration of action of the active substance, by increasing the time of action by gradually passing the core compound through the semipermeable barrier.

In the application of physicochemical and chemical methods, the microencapsulation process depends to a large extent on the stage in which the emulsion of the encapsulated substance is obtained in solution of the particles forming the capsule shell. The emulsification step results in two types of liquid-to-liquid dispersion systems, i.e. emulsions, depending on the encapsulated substance that makes up the core of the capsule and the particles that make up the wall of the capsule. When the core substance is hydrophobic or dissolved in a hydrophobic solvent, and the substance creating the shell material is hydrophilic, most commonly in aqueous solution, the emulsion is oil in water. Conversely, in the

case where the core substance is hydrophilic or dissolved in water, and the compound forming the capsule shell is hydrophobic, or dissolved in a hydrophobic solvent, the resulting emulsion is water in oil.

The entire microencapsulation procedure is performed using effective technologies that provide control of the specific conditions in terms of speed, temperature and pressure, intermittent or continuous agitation. Applying the coacervation as physicochemical method for microencapsulation, a wide variety of shell enclosure materials could be offered, as well as separation methods that could easily be used in the large-scale production. In the complex coacervation, the biopolymer materials are the most suitable for the construction of the microcapsule wall. For instance, gelatin, sodium alginate, gum arabic, chitosan, casein and other biopolymers are the most preferred biomaterials used, which are harmless and build the capsule wall similar to the phospholipids forming the double phospholipid layer of the cell membrane.

During the process of capsule production, before the stage of compound microencapsulation i.e. the shell formation, the core material is dispersed into the emulsion droplets in the solution of the first polyelectrolyte. During the emulsification step, micro droplets are formed, the size of which determines the final diameter of the microcapsules obtained. Independently from the method of production, the droplets size exclusively depends on the reaction conditions i.e. temperature, agitation rate, time [12], as well as the absence or the presence of a surfactant and its variety in concentration [13], and their diameter could vary, changing these condition parameters. Generally, the acidity of the medium (pH) also plays an important role in the microencapsulation process, in the complex coacervation method.

In this work, the rose oil was encapsulated using complex coacervation in the presence of surfactant and applying a variety of solvents, playing the role as media where the basic compound was diluted. Gelatin and sodium alginate were used as one of the possible combinations of the materials forming the wall of the microcapsule. In the case, when an oppositely charged sodium dodecyl sulfate interacts with a polyelectrolyte, the microencapsulation efficiency is high. According to the work of Mayya et al. a primary layer of active polyelectrolyte - surfactant complex is created on the surface, after which a secondary layer of the conjugate polyelectrolyte - polyelectrolyte complex finalizing the two-layer capsule shell wrapping the core material [14]. During the emulsification step, droplets from the core material (encapsulated compound) were formed. Based on these studies, we conclude that SDS plays a crucial role to stabilize the micro-droplets formed on the step of emulsion preparation. Moreover, the solvent has a different and ambiguous effect on the encapsulation efficiency, yield and quality of the microcapsules obtained, in the microencapsulation of rose oil during the complex coacervation process. Nevertheless, study on this parameter will shed light on optimization of these conditions, with a goal - microencapsulation to become economically more profitable.

As was mentioned above, the solvent on the one hand dilutes the expensive materials intended for encapsulation, and on the other hand - affects the encapsulation process, and hence the size, quality and properties of the resulting microcapsules. Due to the importance of the process of microencapsulation of natural products in order to preserve them, through this paper, we studied the dependence of the production of encapsulated rose oil by complex coacervation (properties, quality and size of the resulting microcapsules) on the different solvents.

EXPERIMENTAL

Methods and Materials

The following materials and reagents were used in the current work: formalin (Valerus, Bulgaria) as a 37 % formaldehyde solution and *iso*-propanol (Valerus, Bulgaria); *n*-heptane (C_7H_{16}), *n*-octane (C_8H_{18}), *n*-nonane (C_9H_{20}), *n*-decane ($C_{10}H_{22}$), *n*-undecane ($C_{11}H_{24}$) and *n*-dodecane ($C_{12}H_{26}$) were purchased from Fluka; rose oil was purchased from licensed Bulgarian producers; 10 % NaOH solution, 1N NaOH, and CH_3COOH, Fluka or 10 % citric acid solution were used to adjust the pH throughout the process. The solutions were prepared just before the microencapsulation procedure using the commercial reagents purchased from Valerus (NaOH, $C_6H_8O_7$). Gelatin A (with pI = 9) and sodium alginate (negatively charged throughout the pH range) were purchased from Alpha Aesar. Sodium dodecyl sulfate (SDS) and glutaraldehyde were obtained from Sigma Aldrich.

Preparation of microcapsules

Preparation of microcapsules by complex coacervation using gelatin and sodium alginate as coating material

The preparation of microcapsules was carried out according to the method of Luzzi and Gerraughty [15] as well as Mayya et al. [14], with some own modifications [12, 13, 16 - 18], changing the solvent combined with rose oil as core material. In addition, the process was carried out using an emulsifier 2 % SDS.

General procedure for microencapsulation by complex coacervation using gelatin and sodium alginate as coating material

The solutions of gelatin A (1 % in distilled water) and sodium alginate (1 % in distilled water) were separately prepared as well as the pH was adjusted to pH 6.5 in both of them. 10 mL of 3 % solution of rose oil in the appropriate solvent (C_7H_{16}, C_8H_{18}, C_9H_{20}, $C_{10}H_{22}$, $C_{11}H_{24}$ and $C_{12}H_{26}$) were added to 100 mL of 1 % solution of gelatin A at a temperature of 45°C and a stirring rate of 1000 rpm. After that 2 % SDS were added drop-wise to the mixture. After 30 min. 100 mL of 1 % sodium alginate solution were added (drop-wise) to the obtained dispersion. Distilled water is added to a volume of 210 mL and the obtained mixture is stirred at 45°C. Thereafter, a solution of CH_3COOH or $C_6H_8O_7$ is added to the mixture to adjust the pH to 4.0 - 4.5. At this moment the coacervation process is induced. Stirring is continued for 1.5 h at the same temperature, after that the mixture was cooled to 5 - 10°C in order to coagulate gelatin/sodium alginate system and the cross-linking agent (formaldehyde or glutaraldehyde): 25 - 30 mL of 45 % formalin solution or 50 % glutaraldehyde solution were added to induce reticulation. Finally, pH of the reaction mixture was increased to pH 9 by the addition of NaOH solution and the stirring was continued for 15 hours. The reaction mixture was cooled and the obtained precipitates were filtered, washed with water, water-isopropanol mixture and pure isopropanol. The dehydrated microcapsules were air-dried at room temperature. The precipitate found to settle at the top and bottom of the flask contained the capsules. Moreover, besides microcapsules, at the top and the bottom of the reaction mixture, powder with particles was obtained, leading to lowering the yield of the main product.

Product analysis

The microcapsules were analyzed with a light microscope CARL ZEISS JENA with magnifications of 12.5x, 25x, 40x and 100x. The size of the microcapsules was determined using a reflection microscope NIKON. FT-IR spectroscopic analysis was fulfilled on Perkin Elmer infrared spectrometer model PerkinElmer Spectrum™ 3 MIR FT-IR. FT-IR spectroscopic analysis: infrared spectra of microcapsules, with characteristic absorption spectral maximums of the functional groups of the rose oil are: the OH vibrations of the hydroxyl groups of the essential oils of rose oil are at 1060 cm^{-1}, 1350 cm^{-1}, 1380 cm^{-1}, 1400 cm^{-1}, 3500 cm^{-1}, 3600 cm^{-1}, 3620 cm^{-1} and 3650 cm^{-1}. The oscillations for the C = O groups of the essential oil aldehydes of rose oil are at 1380 cm^{-1}, 1720 cm^{-1}, 1730 cm^{-1}, 1735 cm^{-1}, 2750 cm^{-1} and 2780 cm^{-1}, and from the essential ketones: 1615 cm^{-1}, 1715 cm^{-1} and 1720 cm^{-1}. The characteristic bands for C = C bonds are at 970 cm^{-1} and 1650 cm^{-1}, and C = C-H: 3080 cm^{-1} and 3090 cm^{-1}.

Weight analysis

The yield of the microcapsules (%) is calculated on the basis of the ratio of the total weight of the dried product over the total weight of the raw materials required to form the microcapsules.

$$\text{Yield}\,(\%) = m_1 / (m_2 + m_3)\ \text{x}\ 100\,\% \qquad (1)$$

where: m_1 is the total weight of the microcapsules, m_2 is the starting weight of the encapsulated substance, m_3 is the weight of the starting material used to encapsulate the substance.

$$\text{E\%}_{\text{core.}} = (m_{sp} - m_{sh}) / m_{sp}\ \text{x}\ 100\,\% \qquad (2)$$

where: m_{sp} is the total weight of the sample and m_{sh} is the weight of the insoluble shell.

Another significant parameter, characterizing the microcapsules, is the encapsulation efficiency (yield of the encapsulation compound), which is calculated as the ratio of the weight of the encapsulated material over the total weight of the substance to be encapsulated:

$$\text{Encapsulation efficiency}\,(\%) = (m_a - m_b) / m_{a.}\ \text{x}\ 100\,\% \qquad (3)$$

where: m_a is the total weight of the substance to be

encapsulated, m_b is the weight of the non-encapsulated substance.

RESULTS AND DISCUSSION

In our previous study *n*-decane was used as a starting solvent diluting the rose oil. it was observed that with an increase in surfactant concentration from 0.5 % to 3 %, the range of the average size of the obtained microcapsules decreases from 800 - 600 μm to 220 - 110 μm. The subsequent increasing in this surfactant concentration adversely affects the quality of the microcapsules obtained, including their size, which is enhancing, probably due to agglomeration of the microcapsules.

Effect of the type of solvent

The conditions variability during the process of emulsification plays a key role, especially on the size of the micro droplets, which determines the size of the microcapsules subsequently obtained. As can be seen from Table 1, Fig. 1 and Fig. 4, with solvent changing, i. e. with increasing the length of the hydrocarbon chain from C_7H_{16} to $C_{11}H_{24}$, the capsule size presented by the range of the average capsule size decreases. But further, when C12H26 was used the capsule size was increased (260 - 170 μm), which revealed ambiguous and various properties, depending on the type of the solvent. When *n*-decane was used, the microcapsules size decreased from 230 - 100 μm. The same behavior was observed, when *n*-undecane was employed. But when *n*-dodecane was used to dissolve the rose oil, the range of the average diameter of the microcapsules slightly increases (260 - 170 μm). In turn, from *n*-heptane to *n*-undecane the yield of the capsules and the yield of the encapsulated substance increase (Table 1 and Fig. 2), but the content of the encapsulated substance ($E\ \%_{core}$) from *n*-heptane to *n*-undecane decreases and from *n*-undecane to *n*-dodecane slightly increases (Table 1 and Fig. 2). As the decrease in the values of this magnitude ($E\ \%_{core}$) from *n*-heptane to *n*-undecane indicates that the mass of the encapsulating substance from the insoluble shell is increasing. It follows that the density of the material constituting the shell (the quality of the shell) is increasing. These results show an increase in the amount of pre-polymer adsorbed particles on the surface of the microbeads being formed. The content of the encapsulated substance (*E* % core) increases from *n*-undecane to *n*-dodecane: 21.5 % to 29.9 %, indicating that the mass of the encapsulating substance from the insoluble shell is lowered and from there it follows that the density of the shell material (the quality of the shell)

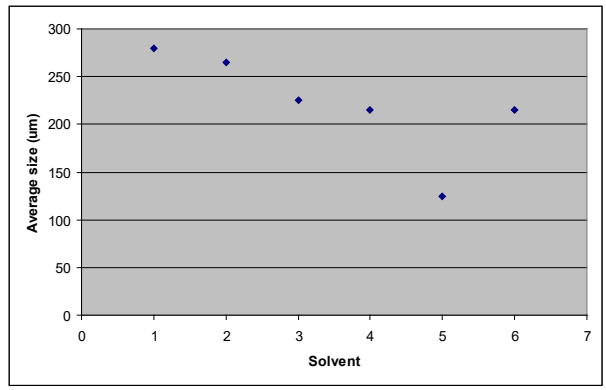

Fig.1. Effect of different solvents on the microcapsules size, presented by the average diameter value (in μm). **1 -** C_7H_{16}, **2 -** C_8H_{18}, **3 -** C_9H_{20}, **4 -** $C_{10}H_{22}$, **5 -** $C_{11}H_{24}$ and **6 -** $C_{12}H_{26}$.

Table 1. Effect of different solvents.

No	Solvent	Yield (%)	Encapsulation efficiency (yield of the encapsulation compound, %)	% sample (encapsulated compound), $E\%_{core.}$	Microcapsules size (range of the average diameter value, μm)
1	C_7H_{16}	18.4	34.7	37.2	330-240
2	C_8H_{18}	21.6	35.7	34.4	310-220
3	C_9H_{20}	27.3	39.3	32.2	280-170
4	$C_{10}H_{22}$	38.7	48.9	21.7	230-100
5	$C_{11}H_{24}$	38.8	51.8	21.5	180-70
6	$C_{12}H_{26}$	34.3	42.2	29.9	260-170

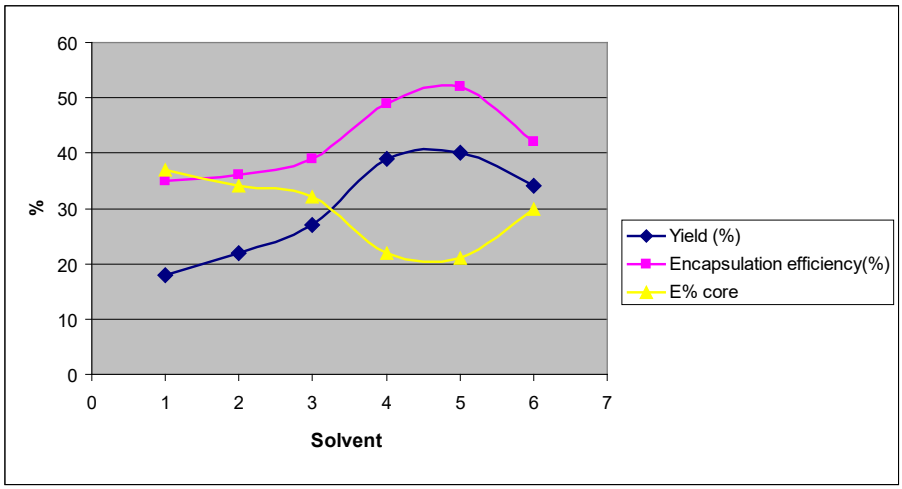

Fig. 2. Effect of different solvents on the yield (%); encapsulation efficiency (yield of the encapsulation compound, %) and % sample (encapsulated compound), $E\,\%_{core}$ of the obtained microcapsules (**1** - **1** - C_7H_{16}, **2** - C_8H_{18}, **3** - C_9H_{20}, **4** - $C_{10}H_{22}$, **5** - $C_{11}H_{24}$ and **6** - $C_{12}H_{26)}$.

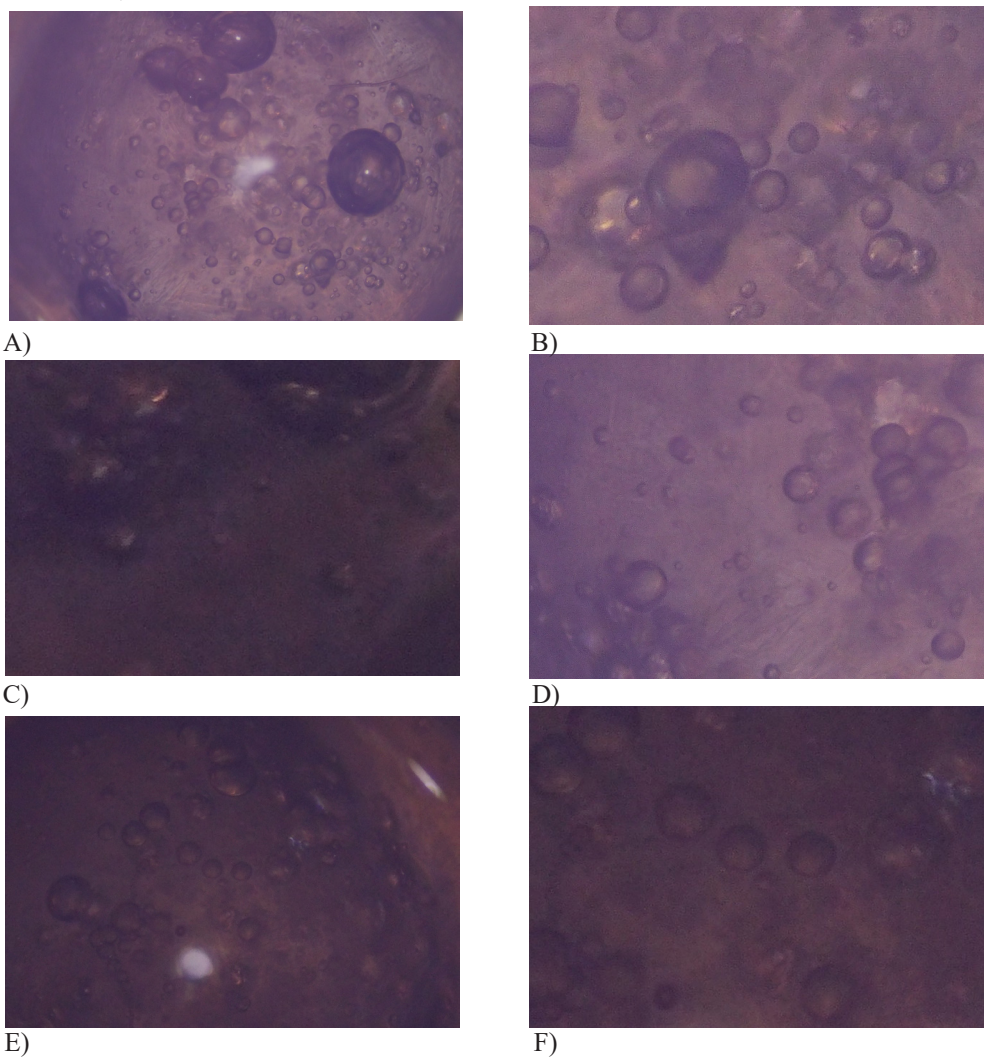

Fig. 3(A). Effect of different solvents on the microcapsules diameter, presented by the digital images, obtained with a reflection microscope NIKON. (A - *n*-heptane; B - *n*-octane; C - *n*-nonane, D - *n*-decane, E - *n*-undecane and F - *n*-dodecane.

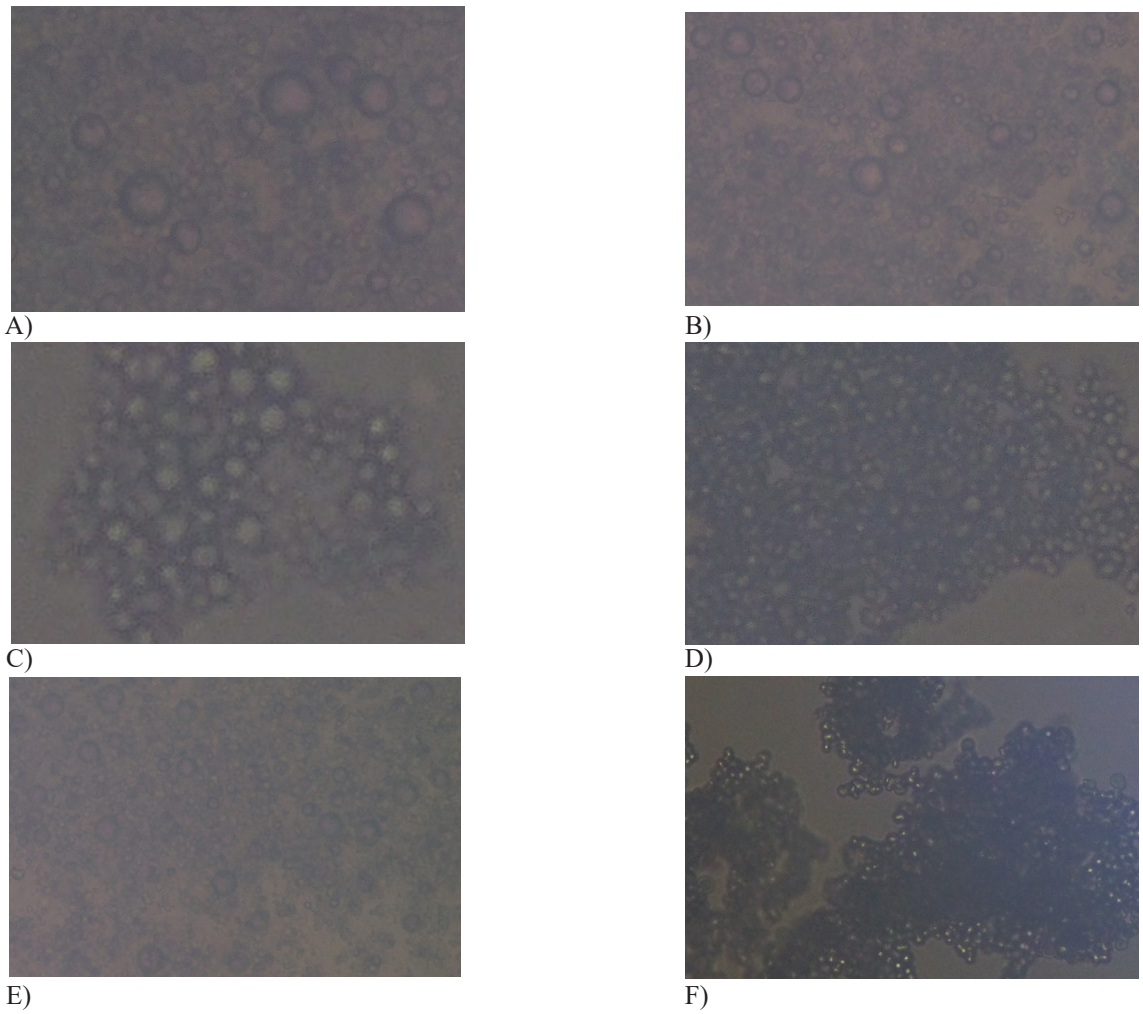

Fig. 3(B). Effect of different solvents on the microcapsules diameter, presented by the optical micrographs, obtained with a light microscope CARL ZEISS JENA with magnification of 40x A - *n*-heptane; B - *n*-octane; C - *n*-nonane, D - *n*-decane, E - *n*-undecane and F - *n*-dodecane.

decreases. Comparing the quality and probably thickness of the microcapsule shell, the following conclusion could be made: from C_7H_{16} to $C_{11}H_{24}$ the quality and density of the shell and probably its thickness increase, while with $C_{12}H_{26}$ the quality and density of the shell, as well as its thickness decrease.

Fig. 3(A) shows the digital images, obtained with a reflection microscope NIKON and Fig. 3(B) reveals the optical micrographs, obtained with a light microscope CARL ZEISS JENA with magnification of 40x.

These preliminary results show the dependence of the quality of the capsule shell on the solvent, and further research will be done in terms of measuring the thickness of the capsule shell, which will provide more conclusive data on the topic.

The obtained results indicate that the most suitable solvents for the rose oil encapsulation process are *n*-decane and *n*-undecane.

CONCLUSIONS

The choice of complex coacervation as a method of microencapsulation is provoked by the fact that due to the unpretentious and inexpensive apparatus used in this case, as well as cheap reagents, this method is easily feasible. In addition, it is not necessary to use chemical polymers that build the capsule shell in some methods of the chemical group, which in turn are obtained during or immediately before the microencapsulation process. This avoids the use of harmful monomers (cyanates and isocyanates)

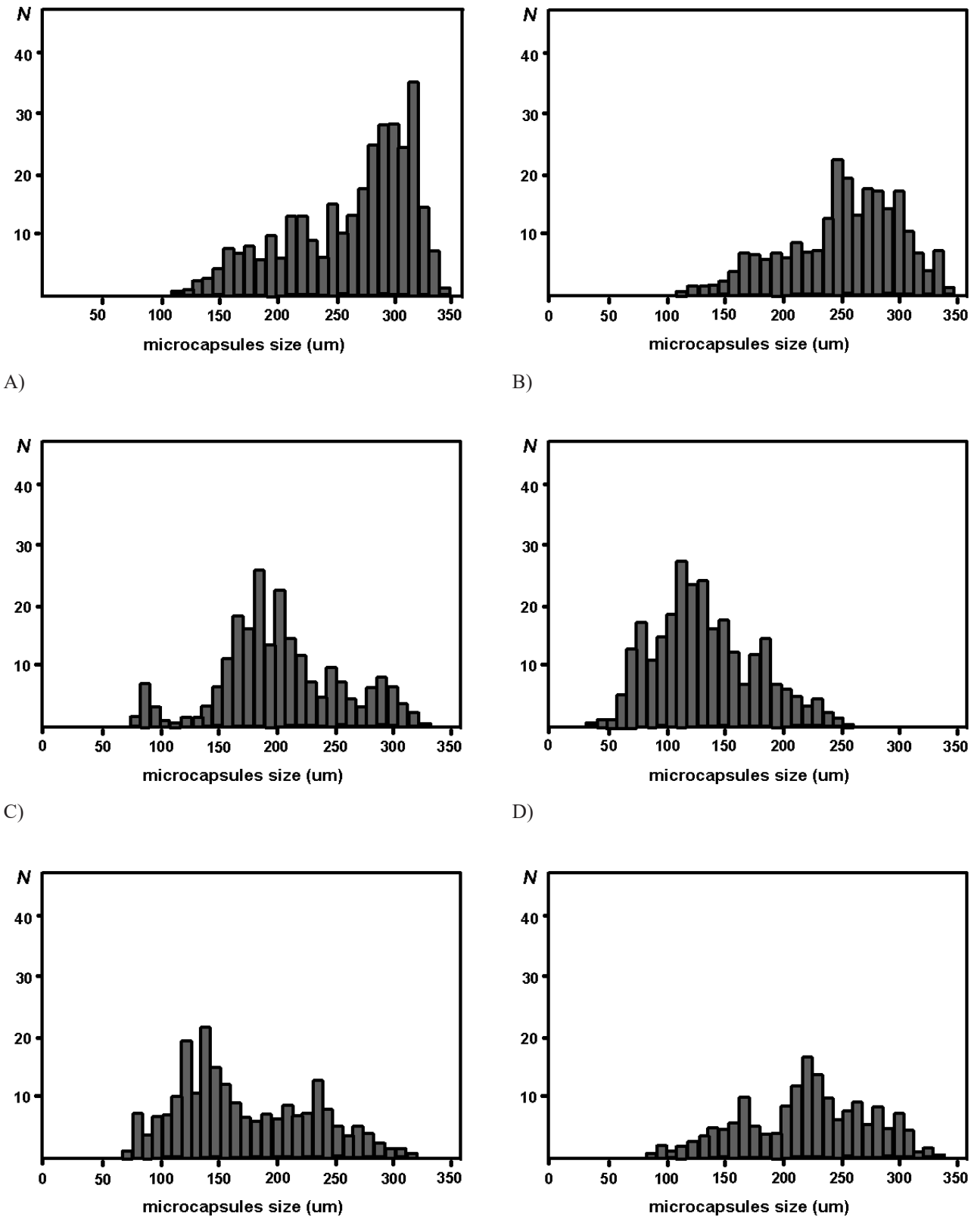

Fig. 4. Effect of different solvents on the microcapsules diameter, presented by the particle size distributions of the obtained capsules. A - C_7H_{16}; B - C_8H_{18}; C - C_9H_{20}, D - $C_{10}H_{22}$, E - $C_{11}H_{24}$ and F - $C_{12}H_{26}$.

and works almost entirely with biological materials. This allows the use of environmentally friendly technology using biodegradable substances [19, 20].

The article considers the influence of the type of solvent on the yield of microcapsules, their size, as well as on the quality of the capsule shell. It was found that with increasing length of the hydrocarbon chain at the solvent (from C_7H_{16} to $C_{11}H_{24}$), the yield raises, as well as encapsulation efficiency (yield of the encapsulation compound, %), while % sample (encapsulated compound, *E* % core) and microcapsules size (described by the average diameter value) decreases. The last two values show that the stability of the microcapsules as well as the quality and density of the capsule shell increase in the same order. Further research will be carried out to measure the thickness of the capsule shell and to provide more conclusive data and evidence of the initial results and interpretations based on them.

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