



## Theory of electrostatic dispersion of polymer solutions in the production of microgel beads containing biocatalyst

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### Abstract

The theory of electrostatic dispersion of polyelectrolyte solutions is elaborated in order to describe the effect of the applied electric potential  $U$  and different physico-chemical factors on the droplet size. It has been shown that the droplet diameters  $d$  gradually decrease with increasing  $U$  as  $d(U) \cong d_0[1 - (U/U_{cr})^2]^{1/3}$  up to some critical value  $U_{cr}$  (ranging between  $\sim 2$  kV and  $\sim 10$  kV). In the region  $U > U_{cr}$  unstable liquid jets begin to form which disaggregate in multiple droplets with diameters smaller than 0.1 mm. The analytical expression for the critical electric potential  $U_{cr}$  as a function of internal diameter  $d_c$  of a needle, distance  $h$  between electrodes, surface tension  $\gamma_0$  of a polymer solution, as well as of viscosity  $\eta$  and flow rate  $j_v$  of polymer solutions, diffusion coefficients  $D$  of surface active species, polarity of applied electric potential and geometry of dropping set-up, and so on, have been obtained. Particularly, it has been shown that the viscosity  $\eta$  as well as the surface tension  $\gamma_0$  have little influence on  $U_{cr}$  when droplets form in non-equilibrium conditions, i.e. when the characteristic time  $\tau_{ad}$  of adsorption of surface active species at the surface of droplets is much greater than the droplet formation time  $\tau_v$ . On the other hand, the sign of the applied electric potential greatly influences the droplets size and  $U_{cr}$ , which is explained

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by the difference in the diffusion coefficients  $D$  and consequently in the time  $\tau_{ad}$  of adsorption at the droplets surface of bulky negatively charged macroions of alginate and small counter ions (e.g.  $\text{Na}^+$ ). © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Microgel beads; Electrostatic dispersion; Polyelectrolyte solutions

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## 1. Introduction

Immobilisation of cells and enzymes by physical entrapment in polymer hydrogels and insoluble interpolyelectrolyte complexes is widely used in bioencapsulation technology [1]. The most widespread is the so-called dropping method consisting in the formation of droplets by pumping polymer solutions containing bioactive substances through a needle and in further solidifying the falling droplets in a receiving solution via ionic or chemical cross-linking, or thermic gelling of polymer. Anionic polysaccharides such as alginates,  $\kappa$ -carrageenan, etc. are often used to obtain hydrogel beads. The ionic cross-linking in a receiving solution is produced by bivalent ( $\text{Ca}^{2+}$ ) or monovalent ( $\text{K}^+$ ) cations. Oppositely charged polyelectrolytes such as poly-L-lysine [2], are used to coat polymeric droplets or hydrogel beads by polymeric membranes via interfacial interpolyelectrolyte complex formation.

The drawbacks of the dropping method are the large size ( $> 1$  mm) of the beads and the low rate of beads formation. Acceleration of the dropletting process and significant decrease of the droplets size may be realised by applying electrical potential to polymer solutions passing through a needle [3]. The hydrogel beads with diameters from 0.1 to 1 mm may be produced by this method [4,5], and the up-grade of the process was considered by increasing flow rates, electric voltage and by utilisation of a multi-needle apparatus [4,6].

The characteristic features of the dispersion of polymer solutions under an electrostatic field are the gradual decrease of droplet diameters  $d$  with increasing the applied difference of potential  $U$  up to some critical electrical potential  $U_{cr}$  and formation of unstable electrized liquid jets with more increase of  $U$  which is

dispersed in multiple droplets with diameters of the order of 0.1 mm and less [3,5]. The values of  $U_{cr}$  range from 2 kV to more than 10 kV depending on numerous physico-chemical and technological parameters such as internal diameter of capillaries (needles)  $d_c$ , flow rate  $j_v$  of polymer solutions through the capillary, concentrations of polymer  $C_p$  and electrolyte  $C_{e1}$ , viscosity of the solution  $\eta$ , polarity of applied electrical potential, geometry of dropping set-up, etc.

In spite of the perspective of this technique for the up-grade in different sectors of the bioencapsulation industry, the mechanisms of the electrostatic dispersion of polymer solutions are still not understood. This makes impossible the construction of an industrial set-up for the production of immobilised biocatalysts and the control of hydrogel beads size. The aim of the present paper is to elaborate a physico-chemical theory explaining and evaluating the effect of mentioned physico-chemical parameters on the unfolding of the dispersion process under applied electrical potential of high voltage.

## 2. Formation of hydrogel beads by simple dropping method

A pendant droplet which is formed by the flow of a liquid through a capillary tube, continuously grows until its mass achieves a critical value  $m$ , at which moment the droplet detaches from the tip of the tube and falls in a receiving solution. In the absence of electric field, the critical mass  $m$  of the droplet may be found from the equilibrium condition

$$mg = \pi d_s \gamma \quad (1)$$

where  $g$  is the gravity constant,  $d_s$  is the diameter of the pendant droplet neck,  $\gamma$  is the surface tension acting at the moment of the droplet detachment (Fig. 1). The volume  $V = m/\rho = \pi \cdot d^3/6$  of a falling droplet may be expressed as a function of the capillary length

$$a = (\gamma/\rho g)^{1/2} \quad (2)$$

by the relationship

$$V = \pi d_s a^2 \quad (3)$$

where  $\rho$  is the effective density of the polymer solution containing bioactive substances, and  $d$  is the diameter of a falling droplet.

The capillary length  $a$  varying in the range of 2–2.5 mm for polymer solutions, the diameter  $d$  of droplets can never be decreased to less than  $\cong 1$  mm in the simple dropping method taking into account that the internal diameters of the capillary needles are commonly ranged from 0.3 to 1 mm in the production of hydrogel beads.

The effect of the flow rate  $j_v$  [ $\text{m}^3 \text{s}^{-1}$ ] of the polymer solution through the capillary tube on the droplet size may be estimated as follows (Fig. 2). At a given

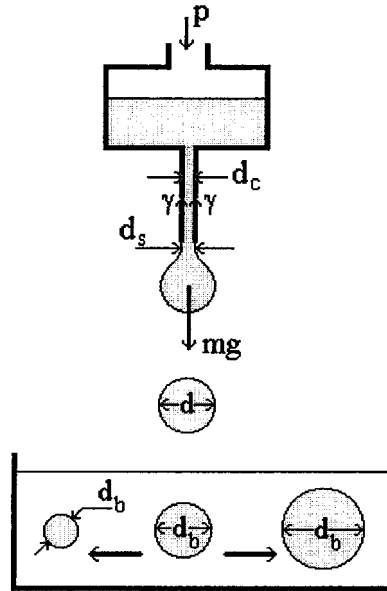


Fig. 1. Scheme representing the formation of hydrogel beads by the dropping method.

value of  $j_v$ , the rate of increasing the area  $A$  of the droplet surface may be expressed from the geometrical considerations as

$$dA/dt = (4/d) \cdot j_v$$

where  $d$  is the effective droplet diameter at the time  $t$ . The adsorption amount of a surfactant at the droplet surface being defined as  $\Gamma = m_s/A$  [mol m<sup>-2</sup>], so the rate of its variation  $d\Gamma/dt$  may be expressed as

$$\begin{aligned} d\Gamma/dt &= (1/A) \cdot (dm_s/dt) - (m_s/A^2) \cdot (dA/dt) \\ &= j_s - (2\Gamma/3V) \cdot j_v = \Gamma \cdot (1/\tau_{ad} - 1/\tau_v), \end{aligned} \quad (4)$$

where  $j_s = (1/A) \cdot (dm_s/dt)$  [mol m<sup>-2</sup> s<sup>-1</sup>] is the flux of the surfactant into the surface under the assumption of its irreversible adsorption,  $\tau_{ad} = \Gamma/j_s$  and  $\tau_v = V/j_v$  are the characteristic relaxation times of the adsorption and of the formation of the drop, respectively.

While, according to Gibbs, the variation (the decrease) of the surface tension  $\Delta\gamma$  is proportional to the adsorption amount  $\Gamma$  of surfactants, one may conclude that for  $d\Gamma/dt > 0$  the surface tension will decrease tending to its equilibrium (minimal) value  $\gamma_e$  at  $j_v \ll (V/\Gamma)j_s$ , i.e. at  $\tau_v \gg \tau_{ad}$ . In the case of  $d\Gamma/dt < 0$  the surface tension will increase and tend to its maximal value  $\gamma_0$  (the surface tension of the pure water) in the limit of  $j_v \gg (V/\Gamma)j_s$ , i.e. at  $\tau_v \ll \tau_{ad}$ .

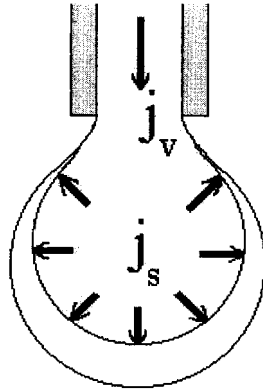


Fig. 2. Scheme illustrating the effect of kinetic factors on the dropping process.

The characteristic time  $\tau_{\text{ad}}$  of the adsorption by the diffusional mechanism may be estimated as

$$\tau_{\text{ad}} = \Gamma/j_s = \Delta x^2/2D = d^2/2D \quad (5)$$

where  $\Delta x$  is the characteristic diffusional length which may be identified with the diameter  $d$  of the droplet, and  $D$  is the diffusion coefficient of the surfactant. When the characteristic adsorption time,  $\tau_{\text{ad}}$ , is much smaller than the characteristic time of droplet formation  $\tau_v$ , the surface tension  $\gamma$  at each instant is equal to its equilibrium (minimal) value  $\gamma_e$ , and the flow rate  $j_v$ , does not influence the droplet diameter which acquires its minimal value  $d_{\text{min}} = (6d_s\gamma_e/\rho g)^{1/3}$  according to Eqs. (2) and (3). On the other hand, when  $\tau_{\text{ad}} \gg \tau_v$ , the surface tension tends to its maximal value equal to  $\gamma_o$ , and liquid droplets acquire their maximal diameter  $d_{\text{max}} = (6d_s\gamma_o/\rho g)^{1/3}$ . In both limit cases, the diameters of the droplets are not affected by the flow rate  $j_v$ . In the whole non-equilibrium range of the variation of the surface tension due to the variation of  $j_v$ , the expected variation of the droplet size cannot be greater than 25% on account that  $d_{\text{min}}/d_{\text{max}} = (\gamma_e/\gamma_o)^{1/3}$  and that the equilibrium surface tension of surfactant solutions  $\gamma_e$  can never be inferior to  $30 \text{ mN m}^{-1}$ .

In the experiments dealing with the production of hydrogel beads, the flow rate  $j_v$  of polymer solutions through the needles ranges from 0.1 to 3 ml/min [4,6]. This corresponds to the characteristic time  $\tau_v$  of droplet formation ranged from 1 to 100 ms for 1 mm droplets diameter. The characteristic time  $\tau_{\text{ad}}$  for the adsorption of low molecular surfactants controlled by their diffusion coefficient  $D$  ( $10^{-8} \text{ m}^2 \text{ s}^{-1}$ ), must be about 100 s. For macromolecular surfactants, the characteristic time of adsorption  $\tau_{\text{ad}}$  will be at least 100 times greater, because of the much larger size of macromolecules. So, the condition  $\tau_{\text{ad}} \gg \tau_v$  is then assessed, and the surface tension of the droplet will then mainly be equal to the one of the pure water  $\gamma_o$ ,

independently of the surfactant component addition to the system. The flow rate  $j_v$  will have little influence on the droplet size  $d$ .

The viscosity  $\eta$  is expected to increase the droplet size while the viscous shear stress  $P_\tau = \eta \cdot (d\varepsilon/dt)$  counterbalances with the surface tension forces (or the capillary pressure  $P_c = \gamma/d_s$  in the drop) the gravitational force  $mg$ . The mean value of the strain rate of the liquid near the neck of the droplet being approximately equal to  $d\varepsilon/dt \cong j_v/d_s^3$ , one can estimate the viscous shear stress as

$$P_\tau = \eta \cdot j_v / d_s^3 \quad (6)$$

Taking into account that for the viscosity  $\eta$  of the polymer solutions ranging from  $10^{-3} \text{ Pa s}^{-1}$  to  $10^{-2} \text{ Pa s}^{-1}$ , and for the flow rate  $j_v$  ranging from 0.1 to 3  $\text{ml min}^{-1}$ , the shear stress  $P_\tau$  ranges from  $10^{-2} \text{ Pa}$  to 1 Pa, one obtains that  $P_\tau \ll P_c$ , while the capillary pressure  $P_c$  is of the order of 50–100 Pa. So, one concludes that the viscosity of the polymer solution has a low impact on the falling droplet size in the conditions of the microgel beads production.

### 3. Formation of hydrogel beads by electrostatic dispersion of polymer solutions

The diameter  $d$  of droplets formed from polymer solutions by dropping method may be significantly decreased by applying the electrical potential  $U$  to the needle [3–5] (Fig. 3).

Fig. 4 presents experimental data concerning the effect of the applied electrical potential  $U$  on the diameters  $d$  of hydrogel beads formed from 0.5% and 1.8% aqueous alginate solutions by the dropping method with two experimental set-ups: composed of a single needle and a plate electrode (curves 1–5), and composed of multiple needles between two parallel plates (curves 6–8). All the experimental dependencies  $d(U)$  are characterised by a sharp decrease of the droplet diameter  $d$  from 2–2.6 mm to  $\sim 0.1 \text{ mm}$  with increasing the electrical potential  $U$  up to some

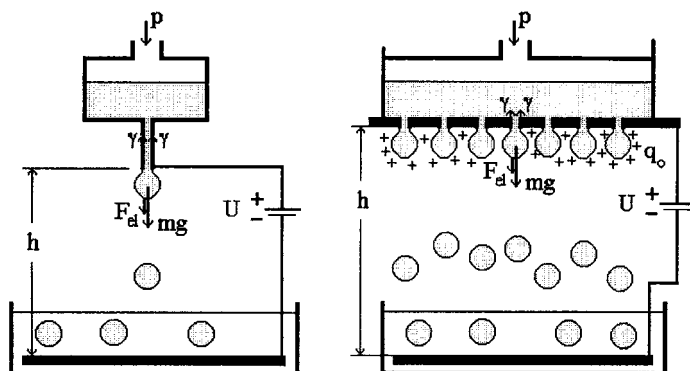


Fig. 3. Scheme illustrating the effect of electric field on the dropping process.

critical value  $U_{cr}$  when unstable liquid jets of polymer solutions begin to form and disaggregate in multiple microscopic charged droplets whose size does not vary with later increase of  $U$  [3,5–7]. The experimental data of Keshavarz et al. [4] obtained for 2% alginate solutions with a 23-gauge needle ( $\sim 0.6$  mm) (curve 5 in Fig. 4) correlate well with the general trends consisting in the decrease of  $d$  with increasing  $U$ . Increasing of the diameters  $d_0$ , corresponding to  $U = 0$ , with increasing the needle diameters  $d_c$  (Fig. 4) is not surprising according to the relationship (3).

In all the experiments with a single needle set-up, the critical potential  $U_{cr}$  did not exceed 5 kV and showed a slight dependence on the needle diameters  $d_c$ . The value of  $U_{cr}$  did not depend on the distance  $d$  between the electrodes and formed the decreasing series (kV): 4.6,  $\sim 4.5$  and  $\sim 4.1$  for the corresponding series of the needle diameters  $d_c$  (mm):  $\sim 0.71$  (22G),  $\sim 0.63$  (23G) and  $\sim 0.50$  (26G), respectively. This dependence correlates in the first approximation with the law  $U_{cr} \sim (d_c)^{1/2}$ .

On the other hand, the experimental data obtained with the multiple needles set-up (curves 6–8 in Fig. 4) are characterized by greater values of the critical electrical potential  $U_{cr}$  varying from  $\sim 8$  kV to  $\sim 12$  kV when the distance  $h$  between the electrodes increases from 25 mm to 48 mm. The dependence  $U_{cr}(h)$  seems to obey the law  $U_{cr} \sim (h)^{1/2}$ .

Fig. 4 proves that for the given geometrical construction of the dropping set-up

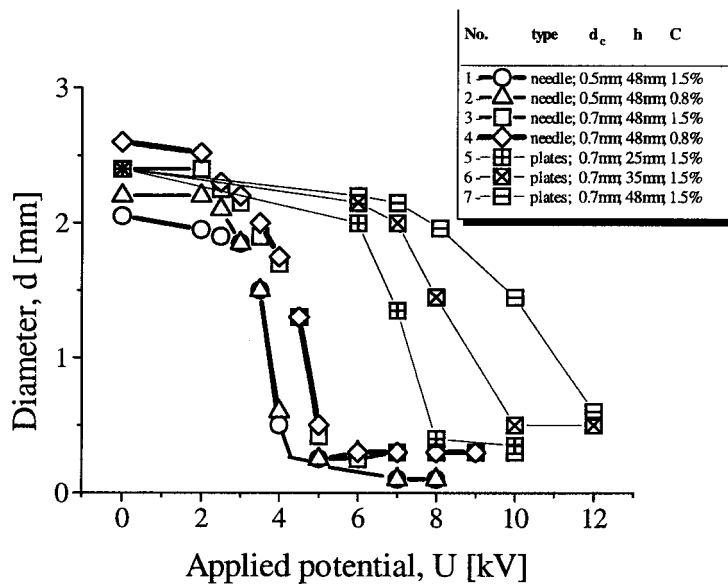


Fig. 4. Effect of the applied electrical potential  $U$  on the gel bead diameter  $d$  obtained by the single needle (curves 1–5) and the multiple needle (curves 6–8) set-ups. The diameter of the needle,  $d_c$  [mm]: 0.71 (3, 4, 6–8); 0.64 (5); 0.50 (1, 2).

the critical electrical potential  $U_{cr}$  manifests very weak sensibility to such physico-chemical parameters as viscosity  $\eta$  (or the concentration  $C_p$ ) and the flow rate  $j_v$  of the polymer solution. In the case of a single needle (Fig. 3a) the value  $U_{cr}$  practically does not depend on the distance  $h$  between the electrodes. So, in this case the internal diameter of the needle  $d_c$  reveals to be the principal factor affecting the droplet diameters  $d$  in the region  $U < U_{cr}$ , other parameters playing an insignificant role in the value of  $d$ . This is obvious when presenting the experimental data of the reduced diameter  $\delta = d/d_0$  as a function of  $U$  (Fig. 5). All the dependencies  $\delta(U)$  (Fig. 5, curves 1–5) practically coincide testifying for the independence of the dropping process under electrical potential  $U$  on such physico-chemical conditions as  $C_p$ ,  $h$  and  $j_v$ .

One has to point out that the diameters  $d_b$  of gel beads in the receiving solutions may differ from the diameters of the falling droplets because of their contraction or swelling in the course of gelling or complex formation processes (Fig. 1). In such a case, the presentation of the experimental dependencies  $d(U)$  in the reduced form  $\delta(U)$  becomes advantageous allowing to neglect this effect and separate the effect of the electrical potential on  $d$  from other factors. In the case of the set-up composed on two plane-parallel electrodes (Fig. 3b), the attention must be drawn on the strong dependence of the process, particularly of the critical potential  $U_{cr}$ , on the distance  $h$  between the electrodes (Figs. 4 and 5).

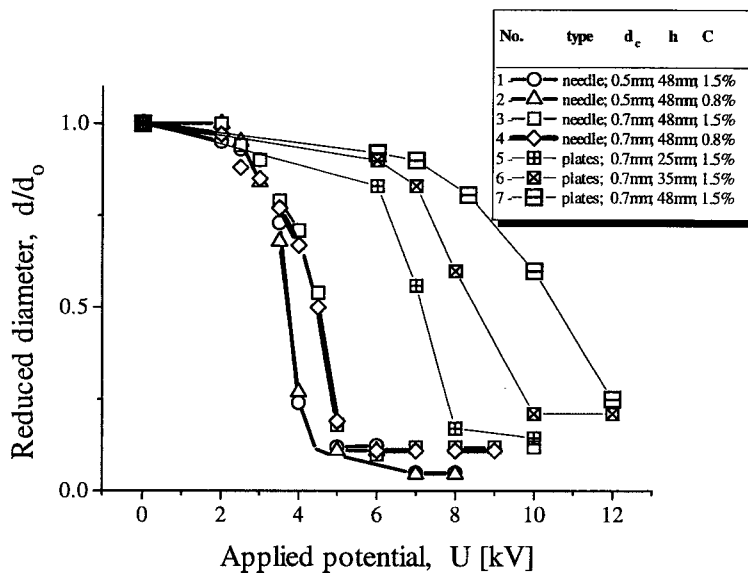


Fig. 5. Effect of the electrical potential  $U$  on the reduced diameter  $\delta = d/d_0$  of gel beads. The diameter of the needle,  $d_c$  [mm]: 0.71 (3, 4, 6–8); 0.64 (5); 0.50 (1, 2). Concentration of the alginate solution,  $C_p$  [%]: 2 (5); 1.5 (1, 3, 6–8); 0.8 (2, 4). Distance between the electrodes,  $h$  [mm]: 48 (1–5, 8); 35 (7); 25 (6).



### 3.1. Electrocapillary effects in the dropping process

In order to elaborate the physico-chemical theory of these phenomena, one has firstly to consider a simplified model of the dropping set-up formed by a needle and a plane electrode situated at the distance  $h \gg d$  below the droplet (Fig. 3a). The equilibrium electrical charge  $q$  accumulated in the system composed by a droplet of diameter  $d$  attached to the tip of a needle of the diameter  $d_c$  is determined by the capacitance  $C$  of this system so that

$$q = C.U$$

with  $C \cong 2\pi\varepsilon_0.d$  for the conducting spherical droplet under the mentioned approximation, where  $\varepsilon_0$  is the permittivity of the vacuum (air).

In the real non-equilibrium process of the droplet formation during the restricted time  $\tau_v = 0.1 \div 1$  s, the capacitance of the system is assumed to be determined essentially by the dimension (the diameter  $d_c$ ) of the extremity of the metallic needle, so the electric charge accumulated by the system will be of the order of  $q = 2\pi\varepsilon_0.d_c$ . Only a part  $q_d = k.q$  is assumed to be localised on the area  $A_d \cong \pi d_c^2$  of the droplet surface, where  $k \leq 1$  is the fitting parameter which accounts for the geometrical and kinetic approximations. In other words, only a part of the equilibrium (maximal) electrical charge will be realised on the droplet under the non-equilibrium conditions, while the characteristic time  $\tau_{ad}$  of the ions adsorption at the droplet surface by diffusion in the electric field is expected to be greater or of the order of the time  $\tau_v$ .

According to Lippman's theory of electrocapillarity (e.g. [8,9]) the equilibrium surface tension  $\gamma$  of the charged surface of a liquid droplet decreases with increasing electrical potential  $U$  as

$$d\gamma = -\sigma.dU, \quad (7)$$

where

$$\sigma = q_d/\pi d_c^2 = 2k\varepsilon_0 U/d_c \quad (8)$$

is the effective surface density of the electrical charge related to the liquid droplet.

Integrating Eq. (7) over  $U$  under the simplifying assumption of its validity in the region  $U < U_{cr}$ , one obtains formally an expression for the decrease  $\Delta\gamma$  of the surface tension in function of the increasing electrical potential  $U$

$$\Delta\gamma = \gamma - \gamma_0^* = -k\varepsilon_0 U^2/d_c,$$

where  $\gamma_0^*$  is the surface tension of the solution at  $U = 0$  and at the given droplet formation time  $\tau_v$ .

Believing that  $\gamma_0^* \cong \gamma_0$  ( $\gamma_0$  is the surface tension of the water) for the assumed non-equilibrium conditions of the droplet formation (otherwise one can write

$\gamma^* = k'\gamma_0$  and account for the kinetic factors), one obtains that the surface tension  $\gamma$  of a droplet submitted to the electrical potential decreases as

$$\gamma(U) = \gamma_0 \cdot (1 - k\varepsilon_0 U^2 / d_c \gamma_0) = \gamma_0 \cdot [1 - (U^2 / U_{cr}^2)] \quad (9)$$

where

$$U_{cr} = \sqrt{d_c \gamma_0 / k \cdot \varepsilon_0} \quad (10)$$

is the critical potential. At  $U \rightarrow U_{cr}$  the surface tension  $\gamma$  tends to zero, and the liquid droplet falls under the action of gravity and electrostatic forces.

The numerical estimation of the critical electrical potential gives the value  $U_{cr} \cong 2.4$  kV for  $\gamma_0 = 72$  mN/m,  $d_c = 0.7$  mm and  $k = 1$ . Despite the difference between the experimental values of  $U_{cr}$  ranging from 4.1 kV to 4.5 kV (Figs. 4 and 5) for the single needle set-up (Fig. 3a), the obtained numerical estimation of  $U_{cr}$  must be considered as rather consistent with the experiment taking into account for rather rough assumptions made of the deduction of the relationship (9) and the approximation  $k = 1$ . According to Eq. (10) the critical value of the electrical potential  $U_{cr}$  does not depend on the distance  $h$  between the electrodes but increases with increasing the diameter of the needle as  $U_{cr} \sim (d_c)^{1/2}$ . One has to point out that both these predictions are verified qualitatively by experiment (Fig. 5).

In the case of a system composed of a multiple number of needles placed in the uniform electric field  $E = U/h$  between two plane-parallel electrodes, we simplified the demonstrations by restricting ourselves to the case of an ideal plane condensator and droplets being born in the vicinity of the upper plate electrode (Fig. 3b). For this system, the density of the electrical charge on the droplets surfaces may be assumed to be equal to the value  $\sigma = k \cdot \varepsilon_0 \cdot E$  of the plate electrode. Proceeding to the analogous integration, we obtained from the Lippman's equation the expression for the surface tension as function of the applied electrical potential in the form

$$\gamma(U) = \gamma_0 \cdot (1 - U^2 / U_{cr}^{*2}) \quad (9')$$

where the critical electrical potential is given now by the relationship

$$U_{cr}^* = \sqrt{h \cdot \gamma_0 / k \cdot \varepsilon_0} \quad (10')$$

The expression (10') predicts the dependence  $U_{cr}^* \sim (h)^{1/2}$  of the critical electrical potential on the distance  $h$  between the electrodes for the set-up represented in Fig. 3b: this has been qualitatively verified (Fig. 5).

### 3.2. Expression for the size of falling droplets in the electric field

The condition for the mechanical equilibrium of a pendant droplet in the electric field may be written in the form

$$mg + F_e = \pi d_s \gamma(U), \quad (11)$$

which accounts for the effect of the applied electrical potential  $U$  on the surface tension  $\gamma$  and for the action of an electrostatic force  $F_e$  on a charged droplet.

The electrostatic force  $F_e$  value depends on the geometric parameters of the experimental dropping set-ups. For example, in the case of a single needle situated in the proximity of an infinite plane electrode (Fig. 3a) one obtains

$$F_e \cong (1/4\pi\epsilon_0).(q_0/2h)^2 \cong \pi\epsilon_0.(d/d_c)^2(d/2h)^2 U^2, \quad (12)$$

where  $h$  is the distance between the droplet and the plane electrode.

For a system composed by several needles placed in the uniform electric field  $E = U/h$  between two plane-parallel electrodes (Fig. 3b) the electrostatic force may be expressed as

$$F_e \cong q_0 \cdot E \cong (\pi\epsilon_0 d^2 U/h).(U/h) \cong \pi\epsilon_0.(d/h)^2 U^2 \quad (12')$$

In spite of the comparatively small value of the electrostatic force  $F_e$  with regards to the gravity force  $mg$  in the region of  $U < U_{cr}$ , its effect on the dropping process is expected to increase considerably near the critical electrical potential  $U_{cr}$ . That is why, the electrostatic force  $F_e$  is included in the mechanical equilibrium Eq. (11).

This equation, in account of Eqs. (2), (3), (10) and (12), may be presented in the case of a single needle set-up (Fig. 3a) in the form

$$d = d_0 \cdot \left\{ 1 - [1 + \alpha_{d/h}].(U/U_{cr})^2 \right\}^{1/3} \quad (13)$$

where

$$d_0 = [6 d_s a_0^2]^{1/3}; \quad a_0 = [\gamma_0/\rho g]^{1/2}; \quad \alpha_{d/h} = (d/d_c)^2(d/2h)^2 U^2 \quad (14)$$

In the same way one obtains the corresponding equilibrium equation for the multiple needles set-up (Fig. 3b)

$$d = d_0 \cdot \left\{ 1 - [1 + \beta_{d/h}].(U/U_{cr}^*)^2 \right\}^{1/3} \quad (13')$$

where

$$\beta_{d/h} = (d/d_c).(d/2h); \quad U_{cr}^* = \sqrt{h.\gamma_0/k.\epsilon_0} \quad (14')$$

The theoretical curves  $\delta(U) = d/d_0$  constructed according to Eq. (13) fit rather well with the corresponding experimental dependencies in the region of  $U < U_{cr}$  (Fig. 5). The fitting parameter  $k$  which accounts for the kinetic and geometric effects on the dropping process was equal to 0.28 whatever the needle diameters  $d_c$  and the distances  $h$  between the electrodes of the single needle set-up.

In the case of a multi-needle set-up (Fig. 3b), the theoretical curves  $\delta(U)$ ,

constructed with the fitting parameter  $k = 3$ , describe well the general trend to decrease the droplet diameter  $d$  with increasing the electrical potential  $U$  (Fig. 5) as well as the increase of the critical electrical potential  $U_{cr}$  with increasing the distance  $h$  between the electrodes according to the law  $U_{cr} \sim (h)^{1/2}$  [Eq. (14')].

Our results concerning the non-dependence of the critical electrical potential  $U_{cr}$  on the distance  $h$  ( $h \gg d_c$ ) between the electrodes in the case of a single-needle set-up (Fig. 3a) does not contradict the data obtained by Nawab and Mason [3]. These authors have found that the value of  $U_{cr}$  for water droplets produced by the dropping method using a single needle set-up with the diameter  $d_c$  of the needle equal to 0.1 mm decreased from  $\sim 3.9$  kV to  $\sim 2.5$  kV with decreasing  $h$  from 1.18 mm to 0.13 mm (Fig. 6).

At relatively large distances  $h \gg d_c$  (when the ratio  $d_c/h \sim 0.1$ ) the critical electrical potential  $U_{cr}$  ceases to vary and becomes independent of  $h$ . This correlates with the relationship (13) in the limit  $h \gg d_c$ . Moreover, at this limit, the value obtained by these authors  $U_{cr} = 3.9$  kV correlates well with theoretically predicted and experimentally verified dependence of the  $U_{cr}$  on the needle diameter  $d_c$  ( $U_{cr} \sim \sqrt{d_c}$ ) (Eq. (10) and the curves 1–5 in Fig. 5).

At shorter distances  $h$ , when  $d_c \sim h$ , the critical potential decreased as  $U_{cr} \sim h^{0.2}$ . This correlates well with Eq. (13) which predicts formally this dependence in the limit  $h \rightarrow d_c$ .

### 3.3. Effect of kinetic factors on pendant droplet formation process in the electric field

In Section 2 we discussed the effect of the kinetic factors on the droplet formation process in the absence of the electric field. It has been pointed out that in the real conditions of the process, the droplets formation time  $\tau_v$  ranging from 0.1 s to  $\sim 1$  s turns out to be much lower than the characteristic time  $\tau_{ad}$  of adsorption by diffusion of surfactants at the interface which is always greater than

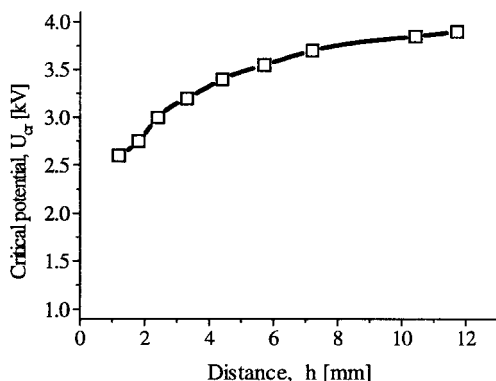


Fig. 6. Effect of the distance  $h$  between electrodes on the critical value of the applied electrical potential  $U_{cr}$  according to the data of Ref. [3].

100 s. It has been concluded that in these obvious non-equilibrium conditions the diameter  $d_0$  of the droplets will be unaffected by the concentration of surface active species in the solution while the surface tension value will remain almost constant and equal to the one of pure water  $\gamma_0$ . So, according to the relationship  $d_0 = [6 d_s a_0^2]^{1/3}$  [Eq. (14)] the droplet diameter will be mainly determined by the needle diameter  $d_c \cong d_s$  while the capillary length  $a_0 = (\gamma_0/\rho g)^{1/2}$  remains constant.

In the electric field, the coefficient of diffusion  $D$  of ionic surfactants is increased in the proportion  $\sqrt{F\Delta U/RT}$ , where  $F$  is the Faraday constant. The relaxation time of adsorption of ionic surfactants and ions  $\tau_{ad}$  must be decreased with increasing the electrical potential  $U$ , and for the case of our interest when the upper limit of  $U$  is of the order of 1 kV to 10 kV, the expected decrease of  $\tau_{ad}$  is of the order  $10^2$  to  $10^3$  times.

For low molecular ionic surfactants and counterions we obtained the relationship  $\tau_{ad} \sim \tau_v$ , that leads to the certain instability of the dropletting process and to the increased sensibility of the droplet size on the flow rate  $j_v$ . Moreover, we may predict that the droplet diameters  $d$  will increase with increasing the flow rate  $j_v$  while the surface tension  $\gamma$  will increase. This conclusion is illustrated by experimental dependencies of the droplet diameters  $d$  on the flow rate  $j_v$  obtained by Keshavarz et al. [4] (Fig. 7). As the flow rate increases, the droplet size also increases and tends to some maximal value determined by the applied electrical potential  $U$  and other parameters.

One has to point out that these experimental data were obtained with the positive pole applied to the needle and the negatively charged grounded plate electrode. The positively charged ions (in our case, the counterions  $\text{Na}^+$ ) are concentrated at the surface of a droplet producing the increase of the surface

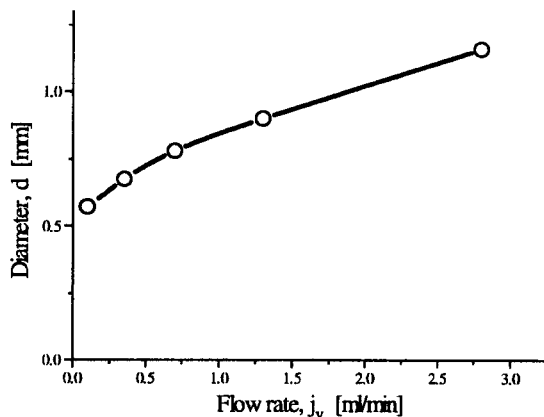


Fig. 7. Effect of the flow rate  $j_v$  of alginate solutions on the mean diameter  $d$  of droplets ( $U = 5$  kV) [4].

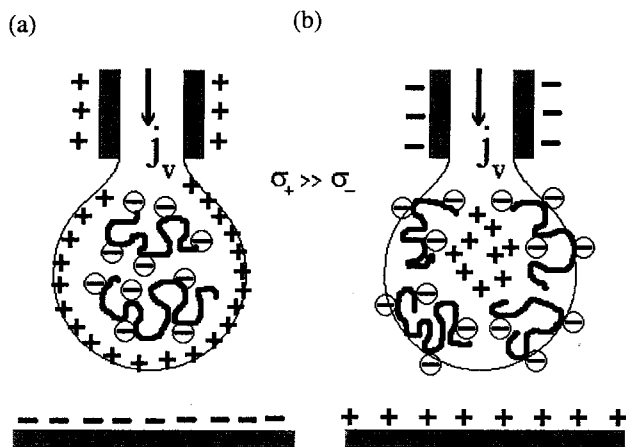


Fig. 8. Scheme illustrating the difference in the adsorption of the positively charged counterions (a) and negatively charged macroions (b) at the interface in an electric field of different polarity.

charge (Fig. 8a) and, consequently, the decrease of the surface tension  $\gamma$  according to the Lippman law [Eq. (7)] and the decrease of droplet size.

When the polarity of electrodes is permuted, i.e. the negative pole is applied to the needle and the plate is charged positively (Fig. 8b), we expect a significant variation in the unfolding of the dropping process. In this case, the negatively charged functional groups of polyelectrolyte (e.g. alginate) will tend to be adsorbed at the surface, whereas the positively charged counterions  $\text{Na}^+$  will tend to go out in the bulk of the solution.

According to the developed theory, we may conclude that the relaxation time  $\tau_{\text{ad}}$  for the bulkier alginate macroions will be much greater than for the ions  $\text{Na}^+$  because of the lower diffusion mobility of the macromolecules with regards to the counterions. For the given electrical potential  $U$  and the flow rate  $j_v$  the surface density of the electrical charge will be lower for the negatively charged needle and, consequently, the surface tension  $\gamma$  will be greater. This will result in a greater droplets size and critical potential  $U_{\text{cr}}$  for the negatively charged needle compared to the positive one. Fig. 9 illustrates these considerations. The experimental curve 1, corresponding to the positive pole on the needle lies far below the curve 2 relating to the opposite polarity of the electrodes.

#### 4. Conclusion

The theory of the electrostatic extrusion and atomisation of polymer solutions from the needle in air to produce microgel beads containing biocatalyst is elaborated. This theory describes the gradual decrease of droplet diameters  $d$  with increasing the applied electric potential  $U$  up to some critical value  $U_{\text{cr}}$  (ranging

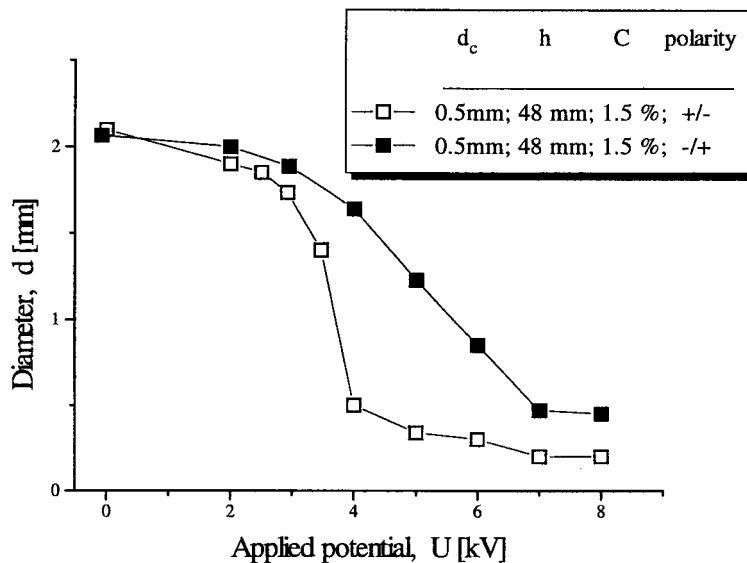


Fig. 9. Effect of the polarity of the electrodes on the curves  $d(U)$ : (1) positive needle–negative solution; (2) negative needle–positive solution.

between  $\sim 2$  kV and  $\sim 10$  kV) and the formation of unstable liquid jets which disaggregate in multiple droplets with diameters smaller than 0.1 mm in the region of  $U > U_{cr}$ .

It has been shown that the critical electric potential  $U_{cr}$  depends on numerous physico-chemical parameters including internal diameter  $d_c$  of a needle, distance  $h$  between electrodes, surface tension  $\gamma_0$  of a polymer solution, as well as on viscosity  $\eta$  and flow rate  $j_v$  of polymer solutions, diffusion coefficients  $D$  of surface active species, polarity of applied electric potential and geometry of dropping set-up, etc. The expressions of  $U_{cr}$  for two set-ups, the first one being a single needle and a plane plate, and the other one being made of two plane-parallel plates, may be expressed, respectively, as

$$U_{cr} = \sqrt{d_c \gamma_0 / k \cdot \epsilon_0} \quad \text{and} \quad U_{cr} = \sqrt{h \cdot \gamma_0 / k \cdot \epsilon_0}$$

where  $\epsilon_0$  is the dielectric permittivity of vacuum, and  $k$  is the parameter whose value depends on the ratio  $\delta = \tau_{ad} / \tau_v$  of the characteristic times of adsorption of surfactants species and of formation of liquid drops, respectively.

It has been shown that in the case of  $\delta = \tau_{ad} / \tau_v \gg 1$  particularly, the viscosity  $\eta$  as well as surface tension  $\gamma_0$  has little influence on  $U_{cr}$ . In contrast, the permutation of electrodes produces a drastic effect on the dispersion process: for the positively charged needle the diameters of droplets were much smaller than for the negatively charged one. This is explained by the difference in the diffusion coefficients  $D$  and consequently in the time  $\tau_{ad}$  of adsorption at the droplets

surface of bulky negatively charged macroions of alginate and small counter-ions (e.g. Na<sup>+</sup>).

We have shown that the droplet diameters  $d$  must decrease with increasing  $U$  as

$$d(U) \cong d_0 \left[ 1 - (U/U_{cr})^2 \right]^{1/3}$$

where  $d_0$  is the droplet diameter at  $U = 0$ . The theoretical curves  $d(U)$  fit well with the corresponding experimental dependences obtained for the alginate hydrogel microbeads containing biocatalysts in different physico-chemical conditions.

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