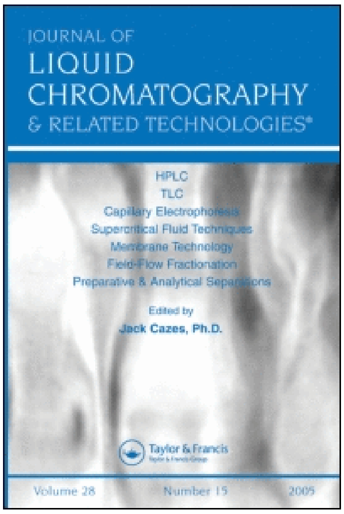

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STUDIES OF LIQUID-LIQUID CIRCULATION

MODELING OF THE HYDRODYNAMIC BEHAVIOR OF TWO NON-MISCIBLE LIQUID PHASES IN A ROTATING COILED COLUMN

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ABSTRACT

A hypothesis of the mechanism of the stationary phase retention in a rotating coiled column has been further developed. Hydrophilic liquid systems have been considered in detail. Incomprehensible earlier peculiarities in their behavior have become rather clear. Starting from the balance of forces of quite different nature acting on two non-miscible liquids in the column, the basic equation of the retention process stability has been derived. Mathematical expressions have been obtained allowing one to estimate, theoretically, the volume of the stationary phase retained in the column, taking into account physico-chemical properties of a liquid system under investigation, and operation and basic design parameters of a planet centrifuge. The experimental data on the retention of the *sec*-butanol - water system support the speculation made.

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INTRODUCTION

Countercurrent chromatography (CCC) utilizes a hydrodynamic behavior of two non-miscible liquid phases in a tubular column space free of a solid support. For over three decades the technique has been successfully applied to the separation and purification of various substances. However, the hydrodynamic phenomena in rotating coils have not been adequately studied and described. In the previous works,[1-3] we have begun to develop (taking into consideration some data[4,5] published by Y.Ito) a mathematical model describing the retention of a stationary phase in a rotating coil.

The hypothesis proposed, is based on consideration of the balance of forces of quite different nature acting on two non-miscible liquids in the coiled column rotating with an angular velocity ω (planetary motion, type J). These are the following:

F_A - Archimedean (buoyancy) force due to the difference between densities ρ_s and ρ_m, $\Delta\rho = \rho_s - \rho_m$, subscripts *s* and *m* correspond to the stationary and mobile phases, respectively;

F_i - inertial force caused by coil motion;

F_η - viscosity force;

F_γ - interfacial tension force;

F_A - adhesion force;

F_h - hydraulic resistance force caused by moving two immiscible phases relative to each other.

For the equilibrium conditions to be fulfilled, the sum of the forces enumerated should be equal to zero, that is, the inertial force should be equal to the sum of the other, counteracting forces:

$$F_i = F_A + F_\eta + F_\gamma + F_w + F_h \tag{1}$$

For the hydrophobic systems, which are characterized by high values of the interfacial tension γ (more than 7 dyn/cm), low values of the viscosity η, and low (a few seconds) hydrodynamic equilibrium settling times, it has been assumed that the stationary phase is retained in the column in the form of discrete "elements" (long large drops) pressed to one tube wall (to the outer one, if the stationary phase is heavier, and to the inner one, if the stationary phase is lighter). The length *L* of an "element" of the stationary phase in a rotating coiled column has been estimated[1]:

$$L \approx \frac{\gamma}{\Delta\rho\sqrt{S}\omega^2 R} \tag{2}$$

where *S* is the cross-sectional area of the stationary phase "element", *R* is the revolution radius of the coiled column, the symbol "≈" (approximately equal to) means proportionality.

The following equation allowed the estimation of the cross-sectional area of the stationary phase "element" for hydrophobic liquid systems:

$$\frac{S}{S_c} \approx 1 - k_1 \frac{\beta^{1/4}}{\omega^{3/4} R^{1/4}} \approx 1 - k_2 \frac{1}{\omega^{3/4}} \qquad (3)$$

where S_c is the cross-sectional area of the coiled column, the rotation radius of the column is designated r; $\beta = r/R$; k_1 is a proportional coefficient characterizing peculiarities of the liquid system (it is dependent on the interfacial tension, viscosity of the stationary phase, and density difference between two phases); $k_2 = k_1 (r^{1/4}/R^{1/2})$.

The ratio of the cross-sectional area of the stationary phase element to that of the coil tube (S/S_c), governs the volume of the stationary phase retained in the column. It has been shown, that the theoretical dependence of S/S_c on the rotation speed ω and the experimental dependence of the S_f value (ratio of the stationary phase retained in the column to the total column volume) on ω for *n*-decane - water and chloroform - water liquid systems, are in qualitatively good agreement. It should be noted, that intermediate phases behave in a rotating coil like hydrophobic phases if β is higher than 0.3. Since most of planetary centrifuges used in practice are characterized by β = 0.4-0.8, the expressions obtained for hydrophobic phases are also valid for intermediate ones. Besides, the model is valid for both lighter and heavier stationary phases.

In the present work, the approach proposed for the describing the hydrodynamic phenomena in rotating coils is being further developed. The behavior of hydrophilic systems, which seemed earlier to be abnormal, will be considered in detail.

THEORETICAL RESULTS AND DISCUSSION

Problem Statement

Hydrophilic liquid systems are characterized by low values of interfacial tension (less than 3 dyn/cm). In this case, the occurrence of discrete stationary phase "elements" becomes impossible. The length of the "element" approaches its radius, that is, the separate "elements" must be linked together to form a continuous layer pressed to one tube wall (to the outer one, if the stationary phase is heavier, and to the inner one, if the stationary phase is lighter). The mobile phase moves at a linear speed, v_m, resulting in the transport of the stationary phase at a linear speed, v_s. The speed difference is $\Delta v = v_m - v_s$. The displacement of phases relatively to each other and the periodical change in the tangential component of the inertial forces, lead to the formation of waves on the interface between two phases.

It should be noted that the dynamics of the macroscopic behavior of the interface between two non-miscible liquids in a rotating coiled column has already been reported to be governed by the evolution of waves.[6] The occurrence of capillary instabilities and its signature were identified with the length of the capillary wave on the interfacial surface (λ_{cap}).

Let us consider, again, a coil rotating with an angular velocity ω (planetary motion, type J). The coil is filled with two non-miscible liquids. Assuming that $\rho_s < \rho_m$ (stationary phase is lighter), then, in the area where the radial component of the inertial forces is minimum, the capillary waves becomes unstable.[7] Droplets break away from their crests and the emulsion process begins. Under these given conditions, the formation of the totality of stationary phase droplets requires a certain period of time. The emulsion formation time (t_e) is the key parameter, which should be taken into consideration, when the stationary phase retention in droplet mode is being described. Now let us consider, in detail, the right part of the coil (Fig.1). The emulsion formation begins at a point *C*. However, before breaking away from the capillary wave crest, the droplet of the stationary phase (entrained by the mobile phase flow) moves along some distance. This distance (CC_1) is dependent on the linear speed of the mobile phase flow and t_e-value. In the left part of the coil, the inertial forces cause the motion

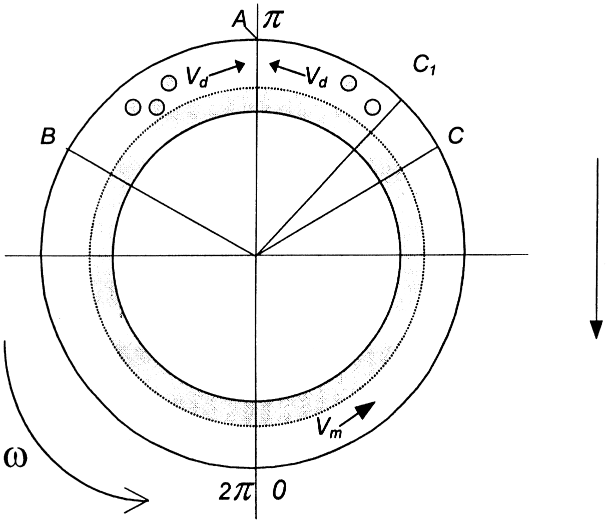

Figure 1. Hypothetical layers of stationary and mobile phases in a rotating coil. $\rho_s < \rho_m$. *BC* - area where the emulsion formation is possible. CC_1 - area where droplets of the stationary phase (entrained by the mobile phase flow) move, before breaking away, together with capillary wave crests.

of droplets in the direction opposite to the mobile phase flow. Consequently, the delay, described above, does not occur.

In other words, the process of the emulsion formation breaks the symmetry of droplets transfer in the left and right parts of the coil. The duration of residence of droplets in the left part of the coil is greater than in the right part. Eventually, droplets of the lighter stationary phase move in the direction opposite to the column rotation and mobile phase flow, whereas, for hydrophobic liquid systems, the direction of the "elements" displacement, column rotation, and heavier mobile phase flow should be the same.[1]

It becomes apparent that, for hydrophilic liquid systems, the heavier mobile phase should be pumped from tail to head to attain the stable retention of the lighter stationary phase, whereas, for hydrophobic systems, the pumping direction from head to tail is required, all other conditions remaining the same. Hence, the behavior of hydrophilic systems (such as *sec*-butanol - water) considered earlier to be abnormal may be explained.

Derivation of the Basic Equation of "Stationarity" for the Droplet Mode

The "stationarity" (stability) term describes the stable retention of a certain stationary phase volume in the rotating coil. It is necessary, for the stable retention of the stationary phase, that the resulting distance (covered by the stationary phase relative to the coil walls per one turn) should be equal to zero:

$$v_s S_s/\omega + (v_m - v_d) t_l S_{\Sigma d} + (v_m + v_d)(t_l - t_e) S_{\Sigma d} = 0 \qquad (4)$$

where v_s and v_m - mean speeds of the stationary and mobile phases, respectively, relative to the tube walls; v_d - mean speed of the stationary phase droplets, relative to the mobile phase flow; S_s - cross-section area of the stationary phase layer pressed to the tube wall; $S_{\Sigma d}$ - cross-section area of the stationary phase layer formed by droplets (if by convention all droplets are combined in one continuous layer); t_l and t_l-t_e - duration of residence of a droplet in the left and right parts of the coil, correspondingly.

The first term in Eq.4 determines the flow (volume per time unit) of the stationary phase moving as a continuous layer along the coiled tube wall, the second and third terms regard the flow of the stationary phase in the form of droplets in the left and right parts of the coil, respectively. Eq.4 can be rewritten:

$$v_s S_s/\omega = v_d t_e S_{\Sigma d} + v_m t_e S_{\Sigma d} - 2 v_m t_l S_{\Sigma d} \qquad (4')$$

Since v_d is much higher than v_m (otherwise, the stationary phase droplets would have been unable to break from the capillary wave crests) the second and third terms in Eq.4′ can be neglected. Consequently

$$v_s S_s/\omega \approx v_d t_e S_{\Sigma d} \quad (5)$$

It should be recalled that, hereinafter the symbol "≈" (approximately equal to) means proportionality.

Estimation of the Emulsion Formation Time and Characteristic Size of a Droplet Breaking Away from the Capillary Wave Crest

If the viscosity of the stationary phase is high (it is inherent in hydrophilic systems), the value of t_e is governed by the forward flow of droplets entrained in the mobile phase. It can be assumed, the inertial forces play the dominant role when the droplets are breaking away from the capillary wave crest. Consequently,

$$F_i \approx F_\eta \quad (6)$$

It is known[7] that, the viscosity force is proportional to the velocity gradient and to the viscosity coefficient (η). The velocity gradient, appearing in movement of stationary phase inside the droplet, is assumed to be proportional to the ratio of the mean moving (redistribution) speed (u) to the diameter of the stationary phase droplet. The inertial forces can be expressed according to the previous publication.[1] Hence,

$$a_r \Delta\rho\, r_d^3 \approx \eta_s (u/r_d)\, r_d^2, \quad (7)$$

where a_r - radial component of the acceleration arising during the rotation; r_d - characteristic size (radius) of the droplet breaking away from the crest; η_s - viscosity of the stationary phase; u - mean speed of the liquid overflow inside the droplet at the instant it is breaking away from the crest, $u \approx r_d/t_e$.

Now Eq.7 can be rewritten to give

$$t_e \approx \eta_s/(\alpha_r \Delta\rho\, r_d) \quad (8)$$

The degradation of the capillary waves occurs when the wavelength λ is close to the critical value λ_{cr}, which is equal to the capillary constant b.

$$b \approx \sqrt{\frac{\gamma}{a_r \Delta\rho}} \quad (9)$$

Considering that the characteristic droplet size corresponds to the capillary constant, it becomes:

$$r_d \approx \sqrt{\frac{\gamma}{a_r \Delta\rho}} \tag{10}$$

It can be obtained from expressions (8) and (10):

$$t_e \approx \frac{\eta_s}{\sqrt{a_r \Delta\rho\, \gamma}} \tag{11}$$

Hence, the time of the emulsion formation is proportional to the stationary phase viscosity, and inversely related to the interfacial tension and density difference between two phases.

According to the definition[4] $a_r = R\omega^2(\cos\theta + 4\beta)$, it seems that droplets break away from capillary wave crests in the relatively narrow area (mixing zone[5]) where the radial component of the inertial forces (in other words, $\cos\theta$) is minimum. Hence, the variation of $\cos\theta$ in the area of interest is insignificant ($\cos\theta \approx -1$). For $\beta > 0.25$, it can be written that $a_r \approx R\omega^2(4\beta - 1)$.

Estimation of Speeds v_s, v_m, and v_d

According to the definition of linear speed

$$v_m = V_p/S_m = V_p/(S_c - S_s) \tag{12}$$

where V_p - mobile phase flow (volume per time unit), S_m - cross-section area of the mobile phase in the coiled column, S_c – cross-section area of the column.

The pressure drop per unit of the column length in the stationary and mobile phase layers is practically the same. It has been demonstrated that Poiseuille's formula can be successfully applied to stratified two-phase flow.[8] Hence, it can be written:

$$v_s \eta_s / S_s = v_m \eta_m / S_m \tag{13}$$

The last two expressions can be transformed to give

$$v_s = \frac{V_p S_s}{(S_c - S_s)^2} \frac{\eta_m}{\eta_s} \tag{14}$$

Also, the interfacial tension force is counterbalanced by a force of hydraulic resistance to the motion of the droplet, which broke away from the wave crest.

$$r_d \eta_m v_d / r_d^2 \approx \gamma / r_d \tag{15}$$

Consequently,

$$v_{\mathrm{d}} \approx \gamma / \eta_{\mathrm{m}} \tag{16}$$

Therefore, the speed of the droplet motion relative to the mobile phase flow, is proportional to the interfacial tension and inversely related to the mobile phase viscosity, that is, the value of v_{d} is governed only by physical parameters of a two-phase liquid system and is not dependent on column rotation speed.

Estimation of $S_{\Sigma\mathrm{d}}$

Assuming that the droplets potential energy in the inertial force field is proportional to the energy expended for moving the droplets across the mobile phase flow (in other words, to the energy extended for overcoming the viscous forces), it can be written

$$S_{\Sigma\mathrm{d}} D\, a_{\mathrm{t}}\;\; \Delta\rho\, H \approx n\, [\eta_{\mathrm{m}} r_{\mathrm{d}} v_{\mathrm{d}} S_{\Sigma\mathrm{d}} / l] \tag{17}$$

where D - conventional unit of the column length; a_{t} - tangential component of the acceleration arising during the rotation, $a_{\mathrm{t}} \approx R\omega^2$; H - distance between the droplet and point A (Fig.1); n - number of droplets per length unit D; l - width of the emulsion (mixing) zone on the interface between continuous layers of stationary and mobile phases (in the limiting case l is equal to the coil diameter); $S_{\Sigma\mathrm{d}}/l$ - mean distance along which droplets move across the mobile phase flow.

Now, the values of H and n can be estimated according to their definitions:

$$n \approx S_{\Sigma\mathrm{d}} D / r_{\mathrm{d}}^{3} \tag{18}$$

$$H \approx R\omega\, t_{\mathrm{d}} \approx R\omega\, d / v_{\mathrm{d}} \tag{19}$$

where t_{d} - droplet life-time which is proportional to the ratio of coil diameter d and droplet linear speed v_{d}.

From expressions (17-19) we can get

$$S_{\Sigma\mathrm{d}} \approx [R^2 \omega^3 \Delta\rho\, d\, l\, r_{\mathrm{d}}^{2}] / [\eta_{\mathrm{m}} v_{\mathrm{d}}^{2}] \tag{20}$$

As is seen from the equation obtained, the cross-section area of the stationary phase layer formed by droplets is proportional to the density difference between two phases, coil diameter, cubed column rotation speed, and inversely related to the mobile phase viscosity.

Estimation of S_{s}

It should be noted that, the volume of the stationary phase retained in the column is determined not only by the cross-section area of the stationary phase layer formed by droplets, $S_{\Sigma d}$, but also by the cross-section area of the continuous stationary phase layer pressed to the tube wall, S_s. These two values are interrelated. However, S_s is eventually predominant. Preparatory to estimating this value from the basic equation of the retention process "stationarity" (Eq.5), the relationship between S_s and emulsion zone width l should be determined. Introducing the following designation:

S_r -ratio of the cross-section area of the stationary phase layer pressed to the tube wall and cross-section area of the coil; $S_r = S_s/S_c$;

The emulsion zone width l is unknown and should be approximated by some function.

There is a lot of different ways of function approximation. The most simple and natural quadratic approximation has been chosen, the assumption made being within the accuracy of the model.

$$l = a_1 + b_1 S_r + c_1 S_r^2 \qquad (21)$$

Taking into account that

$l = 0$ if $S_r = 0$ (column is completely filled by the mobile phase);
$l = 0$ if $S_r = 1$ (column is completely filled by the stationary phase);
$l = d$ if $S_r = 0.5$ (column is filled by the equal volumes of mobile and stationary phases).

On this basis, Eq.21 can be transformed to give

$$l = 4S_r(1\text{-}S_r)d \qquad (22)$$

Now, after a few substitutions, the basic equation of the retention process "stationarity" (Eq.5) can be rewritten

$$\frac{S_r}{(1-S_r)^3} \approx \frac{\omega}{V_p} \frac{R^{1/2} d^2}{(4\beta-1)^{3/2}} \frac{\eta_s^{\,2}}{\Delta\rho^{1/2}\, \gamma^{1/2} \eta_m} \qquad (23)$$

The left part of the equation obtained eventually determines the stationary phase volume retained in the column. Three fractions in the right part regard experimental hydrodynamic parameters, design parameters of the planetary centrifuge, and physico-chemical properties of a liquid system, respectively. Let us consider, in detail, each of these three fractions.

The volume of the stationary phase retained in the column is well known to increase with increasing the rotation speed and decreasing the mobile phase flow rate. As is seen from the first fraction in the right part of Eq.23, this factual evidence is in good agreement with the model proposed.

The second fraction in the right part of Eq. 23, may be the most interesting to interpret the experimental data. It should be noted that, the increase in β-parameter has an adverse effect on the retention of hydrophilic liquid systems,[9] whereas for hydrophobic systems the other effect is observed: the greater is the value of β-parameter, the greater is the retention factor S_f (ratio of the stationary phase volume retained in the column to the total column volume). Incomprehensible earlier peculiarities in the behavior of hydrophilic systems become rather clear. In Eq.23, the value of $(4\beta - 1)^{3/2}$ is in the denominator, that is, according to the model proposed the stationary phase volume retained in the column should decrease with increasing β. The experimental data[9] show that this dependence is actually observed. However, Eq.23 becomes invalid around $\beta = 0.25$ where, clearly, there is a transition between one hydrodynamic behavior to another.

The third fraction in Eq.23 combines several physico-chemical properties of a liquid system. As it is seen from the indices, viscosities of liquid phases may have the most considerable effect on the retention process. Besides, if the more viscous phase is used as the stationary one, the retention factor should be higher. The experimental data[9] on the retention of the *sec*-butanol - water system support the speculation made.

It should be mentioned that the mathematical treatment is valid for rotation speeds about 300 rpm or more, when a stable hydrodynamic equilibrium is attained. If all terms in the right part of Eq.23, except ω, are considered to be constant, it can be written:

$$\frac{S_r}{(1 - S_r)^3} \approx \omega \tag{24}$$

As has been mentioned above, the symbol "≈" means proportionality. Consequently,

$$\frac{S_r}{(1 - S_r)^3} = k_3\omega \tag{25}$$

where k_3 is a proportionality coefficient, which is dependent on the mobile phase flow rate, basic design parameters of a planetary centrifuge, and physical properties of a two-phase liquid system.

The variations of Eq. (25) for $k_3 = 0.1$ are presented in Fig. 2. The experimental dependence[9] of the stationary phase retention for the *sec*-butanol - water system is shown in Fig. 3. As shown by the figures, the theoretical and experimental curves are qualitatively similar.

It would be useful if a series of dependencies described by Eq.23 were studied, in detail, and compared with experimental plots. This is in progress in our laboratory.

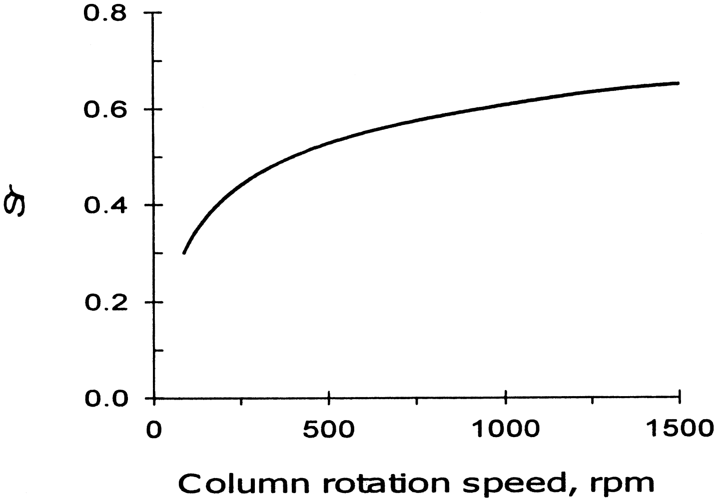

Figure 2. Theoretical ω-dependence of S_r.

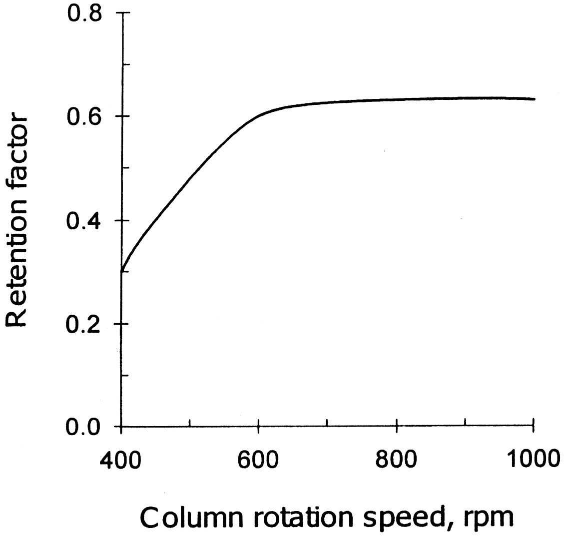

Figure 3. Experimental ω-dependence of the lighter phase retention for *sec*-butanol - water system. $\beta=0.375$. Mobile phase flow rate 1 mL/min.

CONCLUSIONS

A new approach to theoretical investigation on the hydrodynamic behavior of hydrophilic liquid phases in a rotating coiled column has been developed. Occurrence of settling and mixing zones has been explained and mathematically described by degradation of capillary waves on the interfacial surface in the area where the radial component of the inertial forces is minimum.

It has become apparent, why for hydrophilic and hydrophobic liquid systems, the mobile phase should be pumped in opposite directions to attain the stable retention of the stationary phase, all other conditions remaining the same. It has been assumed that, the volume of the hydrophilic stationary phase retained in the column is mainly determined by the ratio of the cross-section area of the continuous stationary phase layer pressed to the tube wall and cross-section area of the coil. This value has been theoretically correlated with operation hydrodynamic parameters, design parameters of the planetary centrifuge, and physical properties of a liquid system. At first glance, the theory and practice are in satisfactory agreement. However, it will be interesting to analyze a series of experimental data obtained by different authors, in order to compare, in detail, the model and factual evidence.

In addition, the model proposed, offers new insights into the hydrodynamic behavior of two non-miscible liquids in a rotating coiled column. The speculation, and some expressions obtained, may be useful for theoretical studies on the behavior of heterogeneous systems (containing colloid and solid particles) in rotating coiled columns.

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