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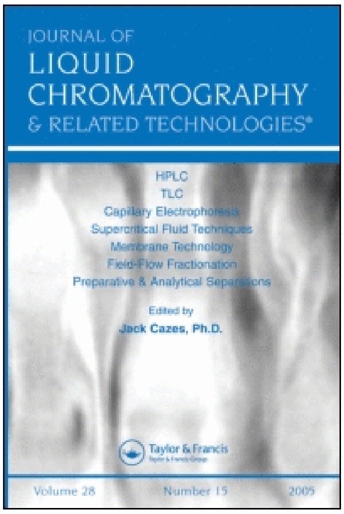

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# ON THE MECHANISM OF STATIONARY PHASE RETENTION IN ROTATING COIL COLUMNS

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## ABSTRACT

A hypothesis of the mechanism of the retention of one (stationary) phase of a two-phase liquid system in a rotating coil column has been proposed. The balance of forces of different nature acting on the stationary phase retained in the coil column has been considered. The basic equation of the retention process stationarity has been derived. Theoretical dependencies of retention factor on rotational speed for hydrophobic systems and experimental data are in good agreement.

## INTRODUCTION

Countercurrent chromatography (CCC) is based on retention (without solid support) of either phase (stationary) of a two-phase liquid system in a rotating column under the action of centrifugal and gravitational forces while the other liquid phase (mobile) is being continuously pumped through.[1] Over three decades the technique has been successfully applied to the separation and purification of organic and bioorganic substances.[2] Since the late eighties some studies on the separation and preconcentration of inorganic substances have been made.[3,4] Various two-phase liquid systems consisting of two, three or more components are used for the separation purposes.

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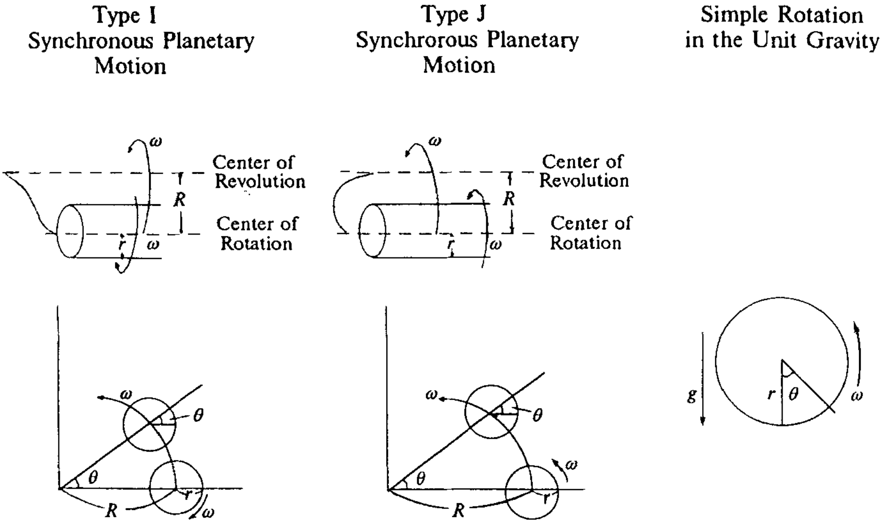

| | Type I | Type J | Simple Rotation |
|---|---|---|---|
| $F_t$ | $R\omega^2 \sin\theta$ | $R\omega^2 \sin\theta$ | $g \sin\theta$ |
| $F_r$ | $R\omega^2 \cos\theta$ | $R\omega^2 (\cos\theta + 4\beta)$ | $g (\cos\theta + r\omega^2/g)$ |

**Figure 1.** Comparative studies on three different rotary systems. $\omega$ - rotation (revolution) speed, $r$ - rotation radius, $R$ - revolution radius, $\beta = r/R$. (Ref. 6, reprinted by permission from Dr. Y.Ito).

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For the last several years, much work has been in progress on developing the CCC theory. Many publications are devoted to the investigation of a force field acting on the rotating coil.[5,7] Simple rotation in the unit gravity and different types of synchronous and nonsynchronous planetary motion have been examined.[5-7] Data on retention of stationary phases has been generalized for a considerable number of two-phase liquid systems. Dependencies of $S_f$ values ($S_f = V_s/V_c$, where $V_s$ = stationary phase volume retained in the column, $V_c$ = total column volume) on the rotation speed ω (synchronous planetary motion) and on the direction and speed of mobile phase pumping have been reported.[7]

A hypothesis of the mechanism of hydrodynamic distribution of two immiscible liquid phases in the rotating coil column has been reported by Ito.[6] The hypothesis is based on the interplay between the force components acting on the fluid in the rotating coil. The tangential force component ($F_t$) generates the Archimedean screw effect, moving two solvent phases toward the head of the coil whereas the radial force component ($F_r$) acts against the Archimedean force. Simple rotation in the unit gravity and two types of synchronous planetary motion have been considered (type I - the coil revolves around the central axis of the device and, at the same time, counter-rotates around its own axis; type J - the coil undergoes a similar planetary motion except that the coil rotates and revolves in the same direction). The values of $F_r$ and $F_t$, acting in point P(x;y) on the coil surface (Fig. 1)[6] can be written as follows:

Type I

$$F_r = R\omega^2 \cos\theta \qquad (1)$$

$$F_t = R\omega^2 \sin\theta \qquad (2)$$

Type J

$$F_r = R\omega^2 (\cos\theta + 4\beta) \qquad (3)$$

$$F_t = R\omega^2 \sin\theta \qquad (4)$$

Simple rotation

$$F_r = g(\cos\theta + r\omega^2/g) \qquad (5)$$

$$F_t = g \sin\theta \qquad (6)$$

In fact, equations (1) - (6) define accelerations.

According to Ito,[6] the multitude of hydrodynamic phenomena observed in the rotating coils can be attributed to the following types of liquid distribution.

1. The basic hydrodynamic equilibrium (the two liquid phases are evenly distributed from one end of the coil, called the head, and any excess of either phase is accumulated at the other end, called the tail).

2. The unilateral hydrodynamic equilibrium (the two solvent phases are unilaterally distributed along the length of the coil, one phase (head phase) entirely occupying the head side and the other phase (tail phase) the tail side of the coil).

It should be noted that most of the conclusions concern the liquid distribution in "closed" columns filled with equal volumes of the lighter or heavier phase and sealed at both ends. Only some comments were made on the

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stroboscopic observations of the lighter stationary phase retention in an "open" column (planet centrifuge of type J). The observation revealed that the column was divided into two zones, the *mixing zone* and the *settling zone*.

Therefore, many questions regarding stationary phase retention in rotating coils still should be answered. The present work is an attempt to develop (taking into consideration the published data)[5-8] a mathematic model describing the hydrodynamic behaviour of the stationary phase in a rotating coil, which could allow us to predict the liquid distribution of a solvent system on the basis of its physical properties and parameters of the experiment. The model concerns the planetary motion of J-type because this motion is most frequently used for the separation of both organic and inorganic compounds.

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## RESULTS AND DISCUSSION

### Problem Statement and Assumptions

Let us consider a coil rotating with angular velocity $\omega$ (planetary motion, type J). The inner diameter of the coil is $d$. The coil is filled with two immiscible liquids; their densities are $\rho_s$ and $\rho_m$ (subscripts $s$ and $m$ correspond to the stationary and mobile phases, respectively). The interphase tension is $\sigma$. The following forces act on an element of the stationary phase, which has the coordinates of its mass center P(x;y) and the length (along a coil) $L$:

$F_A$ - Archimedean (buoyancy) force due to the difference between $\rho_s$ and $\rho_m$; $\Delta\rho = |\rho_s - \rho_m|$

$F_i$ - inertial force caused by coil motion;

$F_\eta$ - viscosity force due to the overflow of the stationary phase element along the coil tube walls;

$F_\sigma$ - interphase tension force;

$F_W$ - 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.

$$F_i = F_A + F_\eta + F_\sigma + F_w + F_h \tag{7}$$

The retention of the stationary phase is possible due to the difference in the densities of the mobile and stationary phases, so that the Archimedean force is a driving one for the retention process.

$$F_A = V \Delta\rho\, a_t \sim L\, S\, \Delta\rho\, a_t \tag{8}$$

where $V$ - volume of a stationary phase element; $S$ - area of the cross section of the stationary phase element, $a_t$ - tangential component of the acceleration arising during the rotation

$$a_t = R\, \omega^2 \sin\theta \tag{9}$$

Henceforward we shall use the symbol "~" to mean the equality with an accuracy of a constant.

To simplify the derivation of a basic model, we assume that the radial forces will be taken into consideration not according to Eq.(3). We reduce the planetary motion to a simple rotation of the coil in a certain force field caused by the revolution and providing an acceleration $g = R\,\omega^2$. In this case, $a_t = g \sin\theta = R\omega^2 \sin\theta$. However, it should be noted that if $\beta>0.25$ (such $\beta$ values provide a stable retention of the stationary phase), $a_r - a_t > 0$ or $F_r - F_t > 0$. Consequently, the stationary phase is always pressed to one tube wall (to the outer one, if the stationary phase is heavier, and to the inner wall, if the stationary phase is lighter).

Let us consider a hypothetical situation: the stationary phase is continuous and forms a "ring" pressed to the coil wall. The Archimedean forces in zones $0 - \pi$ and $\pi - 2\pi$ (Fig. 2) counterbalance each other, but the forces $F_A$ are not compensated at the beginning and at the end of the coil. (Hereinafter $F_A$ - tangential component of the Archimedean forces, acting at a tangent to the coil). The Archimedean forces $F_A$ do not exceed the interphase tension forces $F_\sigma$ till a certain value of angle $\theta$, that is

$$V \Delta\rho R\omega^2 \sin\theta < 2\pi\sigma b L \tag{10}$$

where $b$ is the radius of the stationary phase element.

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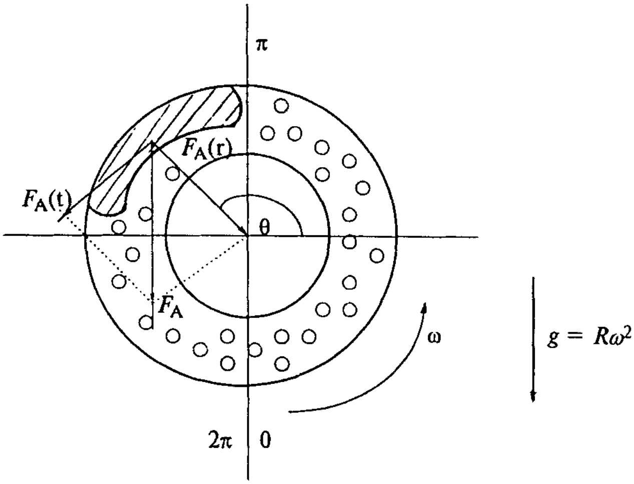

**Figure 2.** Stationary phase element in a coil.

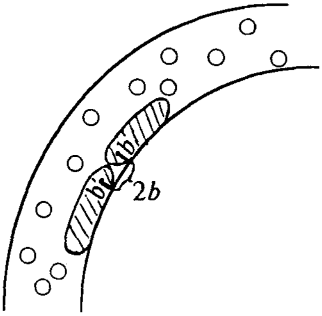

**Figure 3.** Moment of the stationary phase element disintegration.

At a certain value of the length $L$, the inequality (10) changes. The Archimedean forces become stronger than the forces of interphase tension and a part of the element, which had a critical length, breaks off. The disintegration is caused by the work of the Archimedean forces ($A_A$):

$$A_A \sim \Delta\rho\, b\, a_t \sim L\, S\, \Delta\rho\, b\, R\, \omega^2 \qquad (11)$$

On the other hand, the work of the interphase tension forces ($A_\sigma$) can be estimated as following:[9]

$$A_\sigma = \sigma \Delta S \tag{12}$$

where $\sigma$ is the interphase tension coefficient; $\Delta S$ is a change of the two-phase contact surface at a moment of the stationary phase element disintegration. It is not difficult to understand (taking into account the appearance of two additional hemispheric contact surfaces between phases, Fig. 3) that

$$\Delta S \sim 4\pi b^2 - 2\pi b^2 \sim b^2 \quad \text{or} \quad \Delta S \sim S \tag{13}$$

The change of the contact surface between the stationary phase and the tube wall is ignored.

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Let us now consider the time which is necessary for the disintegration of a stationary phase element. This parameter, together with other factors, affects the time for the attainment of hydrodynamic equilibrium. The disintegration time (time from a moment when the Archimedean forces begin to exceed the interphase tension forces to a moment of the stationary phase element disintegration) is dependent mainly on time of moving (redistribution) of stationary phase inside the element just before the disintegration.

At the disintegration moment, the adhesion and density forces are of great importance. The force $F_h$ may be ignored. Hence, the force balance at the disintegration moment can be written as follows:

$$F_i = F_A + F_\eta + F_\sigma + F_w \tag{14}$$

The contribution from the above forces depends on the physical properties (hydrophobicity or hydrophilicity) of the liquid system. Let us consider two most important cases.

1. In the use of hydrophobic two-phase liquid systems (high values of $\sigma$, low values of $\eta$), the interphase tension and adhesion forces are predominant. These systems are characterized by low (a few seconds) hydrodynamic equilibrium settling times[6,8] and, consequently, by low disintegration times.

2. In the use of hydrophilic liquid systems (low values of $\sigma$, high values of $\eta$), the density forces are predominant, that is

$$F_\eta >> F_w, F_i, F_\sigma \tag{15}$$

Therefore (symbol "~" means the equality with an accuracy of a constant),

$$F_A \sim F_\eta \tag{16}$$

These systems are characterized by high values of the time for the attainment of hydrodynamic equilibrium and, consequently, by significant values of disintegration time.

Now equations (8), (9) can be rearranged to obtain

$$F_A \sim V\omega^2 R\,\Delta\rho \tag{17}$$

Hereinafter the expressions for $F_A$ are written with an accuracy of the multiplier $\sin\theta$.

It is known that the viscosity force is proportional to the speed gradient and to the viscosity coefficient ($\eta$). The speed gradient appearing in movement of stationary phase inside the element is assumed to be proportional to the ratio of the mean moving (redistribution) speed ($u$) to the diameter of the stationary phase element. Hence,

$$F_\eta \sim \eta\,(u/s^{1/2})V \sim \eta\,(u/s^{1/2})\,b^2L \tag{18}$$

where $\eta$ - is the coefficient of viscosity. Consequently (Eq. 16),

$$\eta\,(u/s^{1/2})V \sim V\omega^2 R\,\Delta\rho \tag{19}$$

The mean moving speed and the disintegration time $t_0$ can be interrelated by the expression $u = m/t_0$, where $m$ is the distance of the liquid movement. In the case considered, it can be written: $m \sim b$. Since $b = s^{1/2}$, we can get:

$$t_0 \sim \eta/(\omega^2 R\,\Delta\rho) \tag{20}$$

That is, the greater are the rotation speed $\omega$ and the density difference $\Delta\rho$, the less is the disintegration time $t_0$ and, therefore, the less is the time for hydrodynamic equilibrium attainment.

## Derivation of the Basic Equation of Stationarity

The stationarity is termed the stable retention of a certain stationary phase volume in the rotating coil.

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Before deriving the basic equation of stationarity, let us introduce the following designations.

1. $v_d$ - drift speed (the mean speed of the entrainment of stationary phase elements by the mobile phase flow when the column is motionless. This factor characterizes the element motion relative to the wall of a motionless coil column. The drift speed $v_d$ is approximately equal to the mobile phase flow rate $v_m$ if the adhesion and viscosity forces are low.

Hereinafter, absolute speed values are considered.

2. $v_{o\text{-}\pi}$, $v_{\pi\text{-}2\pi}$ - mean speeds of stationary phase element motion relative to a point moving with the drift speed $v_d$ for coil zones $0$ - $\pi$ and $\pi$ - $2\pi$, respectively (Fig. 2). Zones $0$ - $\pi$ and $\pi$ - $2\pi$ are divided by axis $0$ - $\pi$, directions of the axis $0$ -$\pi$ and the vector $g$ are the same.

3. $L_d$ - distance along which a stationary phase element (entrained by the mobile phase flow) moves with the drift speed.

4. $v_r$ - linear motion speed of a point at the coil wall; $v_r = 2\pi r\omega$.

5. $L_\Sigma$ - resultant distance passed by a stationary phase element along to the coil walls in one turn.

6. $t_{o\text{-}\pi}$, $t_{\pi\text{-}2\pi}$ - duration of the residence of stationary phase elements in zones $0$ - $\pi$, $\pi$ - $2\pi$, respectively (right and left parts of the coil).

Further, an average migration of stationary phase elements in zones $0$ - $\pi$ and $\pi$ - $2\pi$ will be considered.

As a consequence of the forces symmetry, it can be written with a sufficient accuracy for our model: $|v_{o\text{-}\pi}| = |v_{o\text{-}2\pi}| = v$.

Hence, $L_\Sigma$ can be expanded in the following terms:

$$L_\Sigma = v\,(t_{\pi\text{-}2\pi} - t_{o\text{-}\pi}) + v_d\,(t_{\pi\text{-}2\pi} - t_{o\text{-}\pi}) + 2v_dL_d/v_r + t_ov_d \qquad (21)$$

The first and second terms in Eq. 21 regard the migration of the stationary phase element in the coil with speeds $v$ and $v_d$, respectively. The third term determines the distance passed by a stationary phase element with the critical length $L$ till the moment of its disintegration. The forth term is the way passed by a stationary phase element within the disintegration time.

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Let us rewrite the third term, taking into account the designation 4:

$$2v_d L_d / v_r = v_d L_d / \pi r \omega \tag{22}$$

The distances passed by the stationary phase elements in zones *0 - π* and *π - 2π* are equal, relative to the fixed coordinate system. Hence, it can be written:

$$L_d + t_o v_r + (v_r + v_d + v)\, t_{\pi\text{-}2\pi} = L_d + (v_r + v_d - v)\, t_{o\text{-}\pi} \tag{23}$$

The term $t_o v_r$ determines the way passed by a stationary phase element with the critical length $L$ within the disintegration time together with the coil wall at the speed $v_r$.

After some algebraic transformations the following expression can be obtained:

$$\frac{t_{0-\pi}}{t_{\pi-2\pi}} = \frac{t_0}{t_{\pi-2\pi}} \frac{v_r}{v_r + v_d - v} + \frac{v_r + v_d + v}{v_r + v_d - v} \tag{24}$$

If effects of the second order insignificance are ignored, Eq. 24 can be rearranged to give:

$$\frac{t_0}{t_{\pi-2\pi}} \frac{v_r}{v_r + v_d - v} \approx \frac{t_0}{t_{\pi-2\pi}} \approx t_0 2\omega \tag{25}$$

Consequently:

$$\frac{t_{0-\pi}}{t_{\pi-2\pi}} \approx t_0 2\omega + \frac{v_r + v_d + v}{v_r + v_d - v} \tag{26}$$

It is necessary, for the stable retention of the stationary phase, that the resultant distance $L_\Sigma$ (covered by a stationary phase element relative to the coil walls per one turn) should be equal to zero. Hence, $L_\Sigma = 0$ is a condition for stationarity. After some algebraic transformations of expressions (21)-(26) and neglecting the parameters of the second order insignificance, an implicit equation for $v$ can be obtained.

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$$v = \frac{v_d^{1/2}\omega^{1/2}r^{1/2}\left[1 + t_o\omega + \frac{t_o v_d}{\pi r} + \frac{v_d}{2\pi r\omega} + \frac{\mathcal{L}_d}{\pi r}\right]^{1/2}}{\left[1 + \frac{2t_o\omega^2 r}{v}\right]^{1/2}} \tag{27}$$

The disintegration time can be expressed as

$$t_o = r\,\varphi/2\pi r = \varphi/2\omega \tag{28}$$

where $\varphi$ - is the angle of disintegration, that is, the angular distance covered by a stationary phase element (more precisely, by its mass center) within the disintegration time. In this case, Eq. 27 may be written in the following form:

$$v = \frac{v_d^{1/2}\omega^{1/2}r^{1/2}\left[1 + \frac{\varphi}{2} + \frac{v_d(\varphi + 1)}{2\pi r\omega} + \frac{\mathcal{L}_d}{\pi r}\right]^{1/2}}{\left[1 + \frac{\varphi\omega r}{v}\right]^{1/2}} \tag{29}$$

Expressions (27), (29) are the main equations of process stationarity. For hydrophobic systems (values of $t_o$ are small, the adhesion forces are insignificant), we may obtain:

$$v \sim v_d^{1/2}\,\omega^{1/2}\,r^{1/2} \tag{30}$$

The correlations (27-30) must be true if a certain stationary phase volume is constantly retained in the rotating coil. The equations obtained will be used for the estimation of the stationary phase element cross section area and other values.

## Estimation of the Length of a Stationary Phase Element

Disintegration of an element with the critical length $L$ is caused by the Archimedean forces work, no matter whether the element is in motion or not.

$$A_A = A_W + A_\sigma \tag{31}$$

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where $A_A$, $A_W$ and $A_\sigma$ are the work of Archimedean, adhesion, and interphase tension forces, respectively.

The Archimedean forces work can be expressed (see Eq. 11) as

$$A_A \sim V \Delta\rho\, 2b\, \omega^2 R \sim L\, b^2 \Delta\rho\, b\, \omega^2 R \tag{32}$$

The adhesion forces work is proportional to the adhesion energy per unit surface ($W_A$), to the length of stationary phase / coil wall contact line and to the distance between contact points[9] (Fig. 3). Therefore,

$$A_W \sim W_A\, 2b\, b \sim W_A\, b^2 \tag{33}$$

The work of the interphase tension forces is proportional to the interphase tension coefficient and to the change in the two-phase contact surface (see Eq. 12):

$$A_\sigma \sim \sigma \Delta S \sim \sigma b^2 \tag{34}$$

Consequently

$$L\, b^2 \Delta\rho\, b\, \omega^2 R = k_1 W_A b^2 + k_2 \sigma b^2 \tag{35}$$

where $k_1$ and $k_2$ are constants.

Then

$$\mathcal{L} \approx \frac{k W_A + k_2 \sigma}{\Delta\rho \sqrt{S}\, \omega^2 R} \tag{36}$$

For the hydrophobic systems (the interphase tension forces significantly exceed the adhesion forces) it can be written

$$\mathcal{L} \approx \frac{\sigma}{\Delta\rho \sqrt{S}\, \omega^2 R} \tag{37}$$

Even in this case, the length of the stationary phase element depends on several parameters. For instance, the greater is the interphase tension, the greater is the element length, and, on the contrary, the greater is the density difference of rotation speed or revolution radius, the less is the length. The value of $S$ is of particular importance, because $S$ and its relationship with $L$ determine the volume of the stationary phase retained in the column. The $S$ value is estimated below.

## Estimation of the Cross Section Area of a Stationary Phase Element

Let us consider the balance of forces, acting on the totality of elements with the length $L$ in the left (right) part of the coil

$$F_i = N\,(F_A + F_\eta + F_w) + F_h \qquad (38)$$

where $N$ is the number of the stationary phase elements in the left (right) part of the coil.

It was shown above that

$$F_A \sim V\omega^2 R\,\Delta\rho;\ \ F_\eta \sim \eta\,(u/S^{1/2})V;\ \ F_w \sim W_A S^{1/2}$$

The force of hydraulic pressure of neighbor stationary phase elements can be estimated on the basis of the following speculations. The totality of elements in the left (right) part of the coil, regardless of $N$, can be estimated as a certain hydraulic ram with cross-section area $S$; the ram moves along the tube wall. Since the liquid is incompressible, the mean flow rate of the mobile phase relative to the tube wall ($v_{rel}$) can be expressed as following:

For the left part of the coil ($\pi$ - $2\pi$):

$$v_{rel} = [(v_s - v_m)\,S] \,/\, (S_c - S) \qquad (39)$$

For the right part of the coil ($0$ - $\pi$):

$$v_{rel} = [(v_s + v_m)\,S] \,/\, (S_c - S) \qquad (40)$$

where $v_m$ - linear speed of the mobile phase flow, $v_s$ - speed of the stationary phase motion relative to the tube wall, $S_c$ - area of the coil tube cross-section.

For the estimation of the forces of hydraulic resistance to the motion of the element totality, a formula known from refs. 10 and 11 can be used. (It should be taken into account that the length of the moving ram significantly exceeds its radius. Interspace between the stationary phase elements is neglected.).

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$$F_h = [\lambda\, L\, v_{rel}^{2}\, (S_c - S)\, N] \,/\, R_k \tag{41}$$

$$R_k = (S_c - S) \,/\, S^{0.5} \tag{42}$$

where $\lambda$ - hydraulic resistance coefficient.

If the flow is laminar (Reynolds number $Re < 2300$)

$$\lambda \sim 1/Re \sim \eta \,/\, [\rho_m v_{rel}\, (S_c^{0.5} - S^{0.5})] \tag{43}$$

For the turbulent flow (Reynolds number $2300 < Re < 10^5$)

$$\lambda \sim 1/Re^{0.25} \sim \eta^{0.25} \,/\, [\rho_m v_{rel}\, (S_c^{0.5} - S^{0.5})]^{0.25} \tag{44}$$

An expression for the hydraulic resistance forces can be obtained after substitution of expressions (40,42,43) in (41).

For laminar flow

$$\mathcal{F}_h \approx \frac{\eta^{0.25}\mathcal{L}\left(u_s \pm u_m\right)\mathcal{S}^{2.25}}{\rho_m^{0.25}\left(\sqrt{\mathcal{S}_c} - \sqrt{\mathcal{S}}\right)^{0.25}\left(\mathcal{S} - \mathcal{S}_c\right)^{1.75}}\mathcal{N} \tag{45}$$

For turbulent flow

$$\mathcal{F}_h \approx \frac{\eta^{0.25}\mathcal{L}\left(u_s \pm u_m\right)\mathcal{S}^{2.25}}{\rho_m^{0.25}\left(\sqrt{\mathcal{S}_c} - \sqrt{\mathcal{S}}\right)^{0.25}\left(\mathcal{S} - \mathcal{S}_c\right)^{1.75}}\mathcal{N} \tag{46}$$

It is possible, now, to estimate the cross-sectional area of a stationary phase element. Let us consider hydrophobic systems most frequently used in CCC. The inertia, density and adhesion forces in these systems are negligibly small in comparison with the Archimedean forces. Therefore, $F_\eta \sim F_A$ and $v_d \sim v_m$. Usually, $\eta_m > \eta_s$ (for instance, for hexane-water, chloroform-water systems). Hence, on the basis of Eq.45 we get

$$\cdot\omega^2\mathcal{R}\Delta\rho\mathcal{V} \approx \frac{\eta\mathcal{L}\left(u_s \pm u_m\right)\mathcal{S}\sqrt{\mathcal{S}}}{\rho_m\left(\sqrt{\mathcal{S}_c} - \sqrt{\mathcal{S}}\right)\left(\mathcal{S} - \mathcal{S}_c\right)} \tag{47}$$

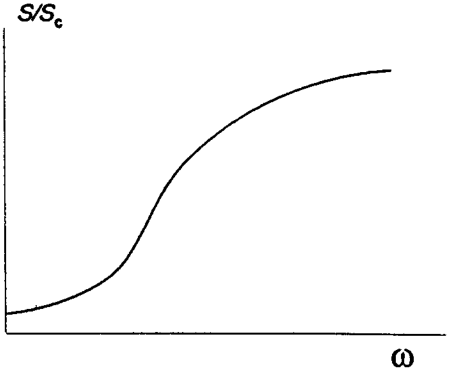

**Figure 4.** Theoretical $\omega$-dependence of $S/S_c$.

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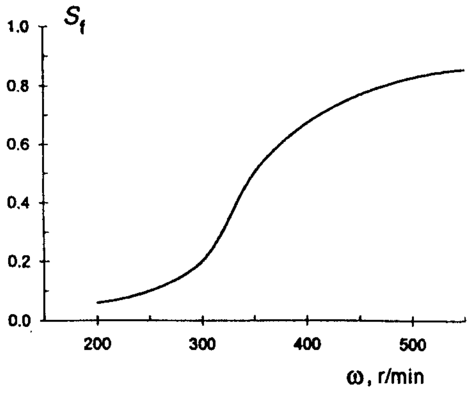

**Figure 5.** Experimental $\omega$-dependence of $S_f$ for *n*-decane - water system. $\beta = 0.37$. Flow rate = 1 mL/min.

According to the definition of mean speed of stationary phase element motion relative to a point moving with the drift speed $v_s \pm v_m = v$. If the values of second order insignificance are neglected, expressions (27) and (46) can be transformed to give:

$$\left(\sqrt{\frac{S_c}{S}}-1\right)\left(S_c - S\right) \approx \frac{v_m^{1/2}\omega^{1/2}r^{1/2}\mu}{\rho_m \Delta\rho \mathcal{R}\omega^2} \qquad (48)$$

If we assume that $S/S_c > 0.5$, Eq.48 can be rewritten (with a sufficient for our model accuracy):

$$\frac{S}{S_c} \approx 1 - k_3 \frac{\beta^{1/4}}{\omega^{3/4}\mathcal{R}^{1/4}} \approx 1 - k_4 \frac{1}{\omega^{3/4}} \qquad (49)$$

where $k_3$, $k_4$ - constants.

The value of $S/S_c$ determines the retention volume of the stationary phase: $v_s \sim s_f \sim S/S_c$. Dependence (49) is presented in Fig. 4.

The theoretical function can be divided into three different parts. In the first one (slow rotation), the ratio $S/S_c$ decreases slowly. Within a certain range of rotational speed $S/S_c$ is almost linearly dependent on $\omega$ (part II). If the rotational speed is further increased, the curve reaches a plateau (part III). We observed a similar dependence when we studied the stationary phase retention in chloroform-water and n-decane-water systems. One of the curves obtained is presented in Fig. 5. Parts II and III can be seen practically in all experimental dependencies of the retention for hydrophobic systems.[7]

It should be emphasized that the expression (49) allows one to judge the influence of rotation and revolution radii and parameter $\beta$ on the retention of the stationary phase in the coil column. As is seen, the greater is the value of $\beta$, the greater is the ratio $S/S_c$ and, consequently, the greater is the volume of the stationary phase retained in the column. On the contrary, the greater is the revolution radius $R$, the less is the ratio $S/S_c$. Therefore, devices with high values of $\beta$ and reasonably low values of revolution radii should be most favorable for the retention of hydrophobic systems. In all, the speculation made is supported by experimental data for systems hexane-water and chloroform-water.[7]

## CONCLUSIONS

A new approach to developing a hypothesis of the mechanism of the stationary phase retention in a rotating coil column has been proposed. For the first time, the balance of forces of quite different nature, acting on the stationary phase element, has been considered. The basic equation of the

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retention process stationarity has been derived. The length of a stationary phase element has been estimated. An expression has been obtained which allows us to estimate the cross-sectional area of a stationary phase element for hydrophobic liquid systems. 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. The theoretical dependence of $S/S_c$ on the rotational speed $\omega$ and experimental dependence of the retention factor $S_f$ on $\omega$ are in good agreement.

Further work is needed to consider, in detail, hydrophilic and intermediate liquid systems, and to describe the droplet mode (dispersion of the stationary phase in the mobile phase and behaviour of the totality of stationary phase droplets forming a stationary phase element).

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## REFERENCES

1. Y. Ito, M. A. Weinstein, I. Aoki, R. Harada, E. Kimura, K. Nunogaki, Nature, **212**, 985-987 (1966).

2. Y. Ito, J. Chromatogr., **538**, 3-25 (1991).

3. Yu. A. Zolotov, B. Ya. Spivakov, T. A. Maryutina, V. L. Bashlov, I. V. Pavlenko, Fresenius Z. Anal. Chem., **35**, 938-944 (1989).

4. E. Kitazume, M. Bhatnagar, Y. Ito, J. Chromatogr., **538**, 133-140 (1991).

5. Y. Ito, Advances in Chromatogr., **24**, 181-226 (1984).

6. Y. Ito, J. Liq. Chromatogr., **15**, 2369-2675 (1992).

7. W. D. Conway, **Countercurrent Chromatography. Apparatus, Theory and Applications**, VCH Publ., New York, 1990.

8. J.-M. Menet . D. Thiebaut, R. Rosset, Anal. Chem., **66**, 168-176 (1994).

9. J. T. Davies, E. K. Rideal, **Interfacial Phenomena**, Academic Press, New York and London, 1961.

10. A. N. Tikhonov, A. A. Samarsky, **Equations of Mathematical Physics**, Nauka, Moscow, 1966.

11. R. Peyret, T. D. Taylor, **Computational Methods for Fluid Flow**, New York, 1984.

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