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Frontal Dynamics of the Sorption of Molecules by Mesoporous Materials of the MCM-41 Type

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Abstract—The sorption of molecules by MCM-41 nanostructured mesoporous sorbents under dynamic conditions is considered. A model of the dynamics of sorption of molecules that considers characteristic features of transport in sorbents, and the kinetic parameter of the ratio between the equilibrium concentrations of dissolved molecules in a solution and the phase of the adsorbent, is presented. The effect the ratio between the rates and characteristic time of the diffusion processes of sorbates in a liquid and a solid body has on the patterns of sorption is shown. The role of the nature of the adsorbent and mobile phase in contact with it is noted, and the effect the solubility and difference between the energy of interaction between the adsorbate and the solvent and adsorbent have on the change in kinetic parameter K and the width of the sorption front is considered as well. The conditions of the change in the width of the sorption front depending on the size of grains and concentration of impurity molecules in the liquid are specified. Limiting cases of the kinetics of adsorption of impurity molecules from solutions are considered.

INTRODUCTION

The emergence of a new class of ordered materials of the M41S family, the most widely used of which are those of the MCM-41 type [1], was quickly followed by their use in catalysis, inorganic chemistry, and supramolecular chemistry [2] due to their narrow pore size distributions; specific surface areas, which are abnormally large for inorganic materials (over 1000 m^2/g); and pore volumes (over 1 cm^3/g). In recent years, the considerable interest in nanostructured materials has been due to their advanced sorption properties [3−9], which find application in medicine [10] and analysis (chromatography) [11−14].

In predicting processes of sorption separation and concentration of substances, we must consider mathematical models of the dynamics of sorption. In considering sorption under dynamic conditions, it is assumed we know the correct shape of the isotherm of sorption in a wide range of concentrations and temperatures. Solutions to problems of the dynamics of sorption are most often considered [15, 16] by assuming linear or nonlinear shapes of the isotherms of sorption and the predominance of the intra- and outerdiffusion or the chemical kinetics of the sorption of substances [17]. The factors determining the shape of chromatograms (i.e., the duration (volume) of elution and the width of the sorption front, which greatly affect the possibility of separating substances similar in nature) therefore vary. Describing the yield curves using asymptotic solutions to problems of the dynamics of sorption [18−21] allow us to consider the kinetic and equilibrium parameters that determine the movement of substances in a sorption system [22−25]. However, such solutions are possible only at long and short process durations. In this work, a solution to the problem of the dynamics of sorption of substances by porous materials with an ordered structure is presented. Characteristic features of the mass transfer of molecules are limitations on pore size (diameter), which determines patterns of the mass transfer of molecules and ions, including organic substances.

The aim of this work was to construct a model and identify patterns of the sorption of molecules by mesoporous solid-body materials in the mode of frontal chromatography. Our consideration of sorption under dynamic conditions assumes we know the correct shape of the isotherm of sorption in a wide range of concentrations and temperatures.

CALCULATION PROCEDURE

We assume that the unit volume of a liquid and a solid adsorbent has g_L and g_S numbers of positions where a dissolved molecule can be in the liquid phase
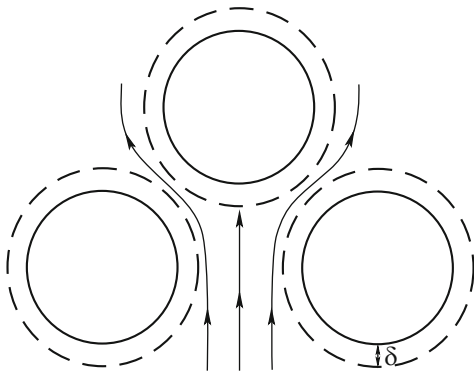
Fig. 1. Flows of a solution of sorbate along the surfaces of grains.

and sorbent, respectively, and n is the average number of molecules present in the allowed position, which is equal to the ratio of the number of molecules of the dissolved substance to the number of positions in the solution. The allowed range of values is $n = (0..1)$. Parameter N has a similar meaning for the adsorbent.

Since no more than one molecule can be present in each allowed position, their average number in the solution is determined by the Fermi−Dirac distribution:

$$n = \frac{1}{\exp\left(\dfrac{E_{\mathrm{L}} - \mu_{\mathrm{L}}}{kT}\right) + 1}, \tag{1}$$

where E_{L} is the energy of interaction between the dissolved molecule and the liquid, and μ_{L} is the chemical potential of the molecule in the liquid.

Similar correlations can also be written for the average number of molecules in the sorbent:

$$N = \frac{1}{\exp\left(\dfrac{E_{\mathrm{S}} - \mu_{\mathrm{S}}}{kT}\right) + 1}, \tag{2}$$

where E_{S} is the energy of interaction between a molecule and an adsorption center in a solid body, and μ_{S} is the chemical potential of the molecule in the sorbent.

Under equilibrium conditions,

$$\mu_{\mathrm{L}} = \mu_{\mathrm{S}} = \mu. \tag{3}$$

We now obtain the correlation between the average occupation numbers of molecules in the positions allowed in the liquid and in solid bodies:

$$p\frac{1 - n}{n} = \frac{1 - N}{N}, \tag{4}$$

where

$$p = \exp\left(\frac{E_{\mathrm{S}} - E_{\mathrm{L}}}{kT}\right) \ll 1, \quad E_{\mathrm{S}} < E_{\mathrm{L}} < 0 \tag{5}$$

is the thermodynamic parameter determining the correlation between the equilibrium concentrations of the dissolved molecules in the solution and adsorbent.

Solving this equation relative to N, we obtain a formula of the Langmuir type [8], written using the equilibrium characteristics of the system:

$$N = \frac{n}{n + (1 - n)p}. \tag{6}$$

We must assume that the period of equilibration between the concentrations of the dissolved molecules in the region of the liquid/grain contact is much shorter than the characteristic duration of sorption. The equilibrium correlation between these concentrations is thus attained in the kinetic process on the surface of the contact. In this case, (4) can be rewritten as:

$$p\frac{1 - n_i}{n_i} = \frac{1 - N_i}{N_i}, \tag{7}$$

where n_i and N_i are the average numbers on the surface of the liquid and solid body in the region of their contact.

Let us consider the diffusion kinetics of dissolved molecules for the flow of a liquid solution through a porous medium. When the liquid flows around the adsorbate particles, conditions for a laminar viscous flow are met. Assuming that the condition of fixation of a substance on the surface of the solid body is met, we find the average gradient of the rate of flow:

$$\mathrm{grad}\, v \cong \frac{V}{r}, \tag{8}$$

where V is the flow rate of the liquid along the channels between the grains, which is determined by the average flow of the liquid, as thus exceeding the average flow rate in the ratio of the area of the column to the area of the channels. Here, r is the size of the channels, which we set roughly equal to the size of the grains. The flow of the liquid breaks down at the distances of individual grains as it travels through the sponge-like medium. The median sections of the flow of the liquid enriched with dissolved molecules lie along the surfaces of the grains as shown in Fig. 1. As a result, the diffusion outflow of the dissolved molecules is accelerated, relative to similar flows in a cylindrical tube. In light of this effect, let us estimate the effective thickness of the diffusion layer through which the dissolved molecules are delivered from the liquid phase to the sorbent.

Average time τ of contact between the liquid and a grain is

$$\tau = \frac{r}{V_i}. \tag{9}$$

In this time interval, the molecules from a layer with the thickness

$$\delta = \sqrt{D_L \tau} = \sqrt{D_L \frac{r}{V_i}}, \qquad (10)$$

where V_i is the speed of the liquid at distance δ from the surface of a grain and D_L is the coefficient of molecular diffusion in the liquid medium. The effective flow rate of the liquid in the near-surface layer is

$$V_i = \text{grad } v\delta = \frac{V}{r}\sqrt{D_L \frac{r}{V_i}}. \qquad (11)$$

We now find the thickness of the diffusion layer:

$$\delta = \left(\frac{D_L r^2}{V}\right)^{1/3}. \qquad (12)$$

The diffusion density of the flow under these conditions is

$$j_1 = \frac{D_L S}{\delta}(n - n_i) = \frac{D_L^{2/3} V^{1/3} S}{r^{2/3}}(n - n_i). \qquad (13)$$

Here, S is the surface area of the adsorbate grains in contact with the solution per unit volume ($[S] = 1/L$).

Note that for slow flow rates ($\delta = r$), $\tau = \dfrac{r^2}{D_L}$. Our mathematical model of the kinetics of adsorption can now be presented in the form:

$$\frac{\partial n}{\partial t} = -\frac{D_L S}{\delta}(n - n_i) - V\frac{\partial n}{\partial z}, \qquad (14)$$

$$\frac{\partial N}{\partial t} = -\frac{D_S}{r^2}(N - N_i). \qquad (15)$$

Here, $\dfrac{\partial n}{\partial t}$ is the rate of the change in the average number of dissolved molecules in the liquid, $\dfrac{\partial N}{\partial t}$ is the rate of capture of the molecules by the sorbent grains, and $\dfrac{\partial n}{\partial z}$ is the change in the concentration in a layer along the z coordinate.

The second summand of (14) considers the change in the local concentration of the liquid when there is a flow. Equation (15) is obtained by assuming that the molecules rate of capture is determined by their diffusion from the surface of the grains to its volume. The final stage of this process is considered, at which it is characterized by the period of relaxation:

$$\tau_S = \frac{r^2}{D_S}. \qquad (16)$$

Note that Eqs. (14) and (15) are combined into a system of equations by boundary condition (7), which reflects the equilibrium of a system of molecules in a narrow near-boundary layer.

Let us obtain another boundary condition from the equality of the flows of dissolved molecules, i.e., the flow entering from the liquid phase and the flow traveling from the surface of a grain to its bulk:

$$g_L \frac{S D_L}{\delta}(n - n_i) = g_S \frac{D_S}{r^2}(N - N_i). \qquad (17)$$

This correlation is written as:

$$n - n_i = -K(N - N_i), \qquad (18)$$

where:

$$K = \frac{g_S}{g_L}\frac{D_S}{D_L}\frac{\delta}{S r^2}, \qquad (19)$$

where g_L and g_S are the numbers of the positions for the adsorbed molecules per unit volume of the liquid and adsorbate, respectively.

Dimensionless coefficient K determines the correlation between the rates and characteristic time τ of the diffusion of impurity molecules in a liquid and solid body. Helfferich and Hwang [24] showed that quantity He, which characterizes the rates of external and internal diffusion, is a simple criterion of attribution to outer- or intradiffusion kinetics. Parameter K is in its physical sense similar to diffusion criterion δ^*, which characterizes the contribution from external and internal diffusion to the kinetics of the sorption of ions. For a sorbent medium in which the Henry law is obeyed (the case of linear isotherm $\Gamma = dN/dn = \text{const}$), it is written as Biot criterion (Bi) [25, 26]

$$Bi = \frac{\beta R^2}{\bar{D}\Gamma}, \qquad (19a)$$

where $\beta \equiv D_L/d$ is a kinetic coefficient characterizing the diffusion in the solution near the surface of the sorbent and $\bar{D} \equiv D_S$ is the coefficient of diffusion in the phase of the sorbent.

In expression (18), ratio g_S/g_L can describe the Henry constant in the case of a linear isotherm of sorption or a derivative characterized by the value of the coefficient of distribution in the case of a nonlinear isotherm of sorption. Parameter K in formula (18) generally has a physical sense similar to the Helfferich [24, 25] and Biot [19–21] diffusion criterion.

It is important to consider the effect the character of the change in the specified parameter has on the dynamics of sorption, i.e., the elution of the sorbate in the yield curves, and on the width of the sorption front. Low values of K testify to the relative slowness of diffusion inside a solid body. The solution to a problem of the dynamics of sorption is often found under the conditions where there is no limitation on intradiffusion, which simplifies finding an analytical solution. Below, we consider a case where K has a fairly high value, i.e., $K \gg p$ and n_0. Note that since K falls as the flow rate of the solution rises (see Eq. (12)), the process that controls sorption from diffusion in a liquid to diffusion in a solid body can change.

The solution to system (14), (15) is sought in the form of a sorption front moving at rate υ in the direction of the flow of a liquid solution:

$$n(t, z) = n\left(t - \frac{z}{v}\right), \quad N(t, z) = N\left(t - \frac{z}{v}\right) \quad (20)$$

is substituted into system (14), (15), and we obtain the expression

$$\left(1 - \frac{V}{v}\right)\frac{dn}{dt} = -\frac{D_L S}{\delta}(n - n_i), \quad (21)$$

$$\frac{dN}{dt} = \frac{D_S}{r^2}(N - N_i). \quad (22)$$

From system (21), (22), we obtain:

$$\frac{dN}{dn} = \frac{V - v}{v}\frac{g_L}{g_S}. \quad (23)$$

Solving this differential equation in a linear dependence throughout the range of concentrations:

$$N = Un, \quad (24)$$

$$U = \frac{V - v}{v}\frac{g_L}{g_S}. \quad (25)$$

Formulas (24) and (25) allow us to find the expression for the sorption front's rate of movement. We assume there is an equilibrium distribution between the adsorbate molecules in the liquid and adsorbent away from the front $(z \to -\infty)$, and we obtain from (7):

$$p\frac{1 - n_0}{n_0} = \frac{1 - Un_0}{Un_0}, \quad (26)$$

where n_0 is the initial ratio of the number of the dissolved molecules to the number of positions in the solution:

$$U = \frac{1}{n_0 + p - n_0 p}. \quad (27)$$

Substituting (27) into (25) and solving the resulting equation relative to v, we find that

$$v = \frac{(n_0 + p)g_L}{g_S + g_L(n_0 + p)}V. \quad (28)$$

An important case in the separation of substances is that of low concentrations of dissolved molecules $(n_0 \ll 1)$. Since condition $p \ll 1$ is required for sorption, simpler formulas are obtained from (27) and (28):

$$U = \frac{1}{n_0 + p}, \quad (29)$$

$$v = \frac{g_L(n_0 + p)}{g_S}V. \quad (30)$$

To solve system (21) and (22), we first find the correlation between n and n_i using (7) and (18):

$$n = n_i\frac{(p + K + n_i)(p + n_0)}{(p + K + n_0)(p + n_i)}. \quad (31)$$

The solution to Eq. (31) relative to n_i is a fairly cumbersome function, so it cannot easily be substituted into Eq. (21). The variable in the equation itself is therefore replaced by assuming that n_i is an unknown function:

$$\frac{dn_i}{dt} = \frac{1}{\tau_S}\frac{(n_i + p)n_i(n_0 - n_i)}{(Kp + p^2 + 2pn_i + n_i^2)}. \quad (32)$$

The solution to this equation is written in the cumbersome but manageable form:

$$\frac{t}{\tau_S} = \frac{(K + p)}{n_0}\ln(n_i) - \frac{(Kp + n_0^2 + 2n_0p + p^2)}{n_0(n_0 + p)}$$
$$\times \ln(n_0 - n_i) - \frac{K}{n_0 + p}\ln(p + n_i). \quad (33)$$

Formulas (31) and (33) determine parametric dependence $n(t)$, in which n_i is a parameter that varies in the range of $(0...1)$.

Let us consider limiting cases of the kinetics of separation of impurity molecules. With relatively slow diffusion in a solid-phase medium, i.e., when $K \ll p$ and n_0, we find from (31) and (32):

$$n = n_i, \quad \frac{dn}{dt} = \frac{1}{\tau_S}\frac{n(n_0 - n)}{p + n}. \quad (34)$$

Setting τ_S as the characteristic period of adsorption in (34) and introducing new variables

$$n = n_0 f, \quad (35)$$

$$\frac{z}{\lambda} \to z, \quad (36)$$

$$q = \frac{p}{n_0}, \quad (37)$$

where λ is the width of the front and f varies in the range of $(0...1)$, we obtain Eq. (34) in the form

$$\frac{df}{dt} = \frac{f(1 - f)}{q + f}. \quad (38)$$

Parameter q, which can vary over a wide range, characterizes the condition of the saturation of the adsorbent by sorbate molecules. Setting $N \cong 1 = \frac{n_0}{p} = \frac{1}{q}$, we find the condition of saturation is fulfilled at low values of parameter $q \ll 1$ (Fig. 2a).

The solution to Eq. (38) depends solely on parameter q. At high values of this parameter that correspond to fairly low concentrations of impurities in the liquid phase, Eq. (38) is written as

$$\frac{df}{dt} = \frac{f(1 - f)}{q}. \quad (39)$$

The solution to (39) meeting boundary conditions $f(\infty = 1)$ and $f(-\infty) = 0$ is written as

$$f = \frac{1}{1 + \exp\left(\dfrac{-t}{q\tau_S}\right)}. \tag{40}$$

It has an asymmetric shape with inversion point $f = 1/2$. The width of the front,

$$\lambda = Vq\tau_S \tag{41}$$

grows upon a reduction in the concentration of molecules (Fig. 2b). When q falls upon a drop in temperature or a rise in n_0, Eq. (39) in the extreme case where $q \to 0$ acquires the simple form

$$\frac{df}{dt} = 1 - f. \tag{42}$$

Its solution can be written as

$$\begin{aligned} f &= 1, \quad t > 0; \\ &\exp(-t/\tau_S), \quad t < 0. \end{aligned} \tag{43}$$

The adsorption front shrinks exponentially and has the characteristic width

$$\lambda = V\tau_S. \tag{44}$$

It therefore shrinks exponentially and has a minimum for the considered width conditions that is determined by the characteristic period of diffusion for molecules inside the grains.

In another limiting case of high values of K (Fig. 2, curve 2), we find from (31) that

$$n_i = \frac{pn}{p + n_0 - n}. \tag{45}$$

Substituting (45) into (21) gives us

$$\frac{dn}{dt} = \frac{(p + n_0)}{\tau_L} \frac{n(n_0 - n)}{(p + n_0 - n)}, \tag{46}$$

$$\tau_L = \frac{\delta}{D_L S} = \frac{r^{2/3}}{V^{1/3} D_L^{2/3} S}. \tag{47}$$

Substituting variables $t/\tau_L \to t$, we obtain

$$\frac{df}{dt} = n_0(q + 1) \frac{f(1 - f)}{(q + 1 - f)}. \tag{48}$$

The characteristic width of the front is then

$$\lambda = \frac{V\tau_L}{(n_0 + p)} = \frac{V^{2/3} r^{2/3}}{(n_0 + p) D_L^{2/3} S}. \tag{49}$$

The width of the front therefore grows along with the flow rate of the liquid solution and the size of the grains according to an exponential law. The asymmetry of the front also grows along with parameter p.

An accurate solution to (33) must be used in the transitional region of parameters where the mechanism controlling the process of adsorption changes from diffusion in grains to diffusion in liquids (Fig. 2c).
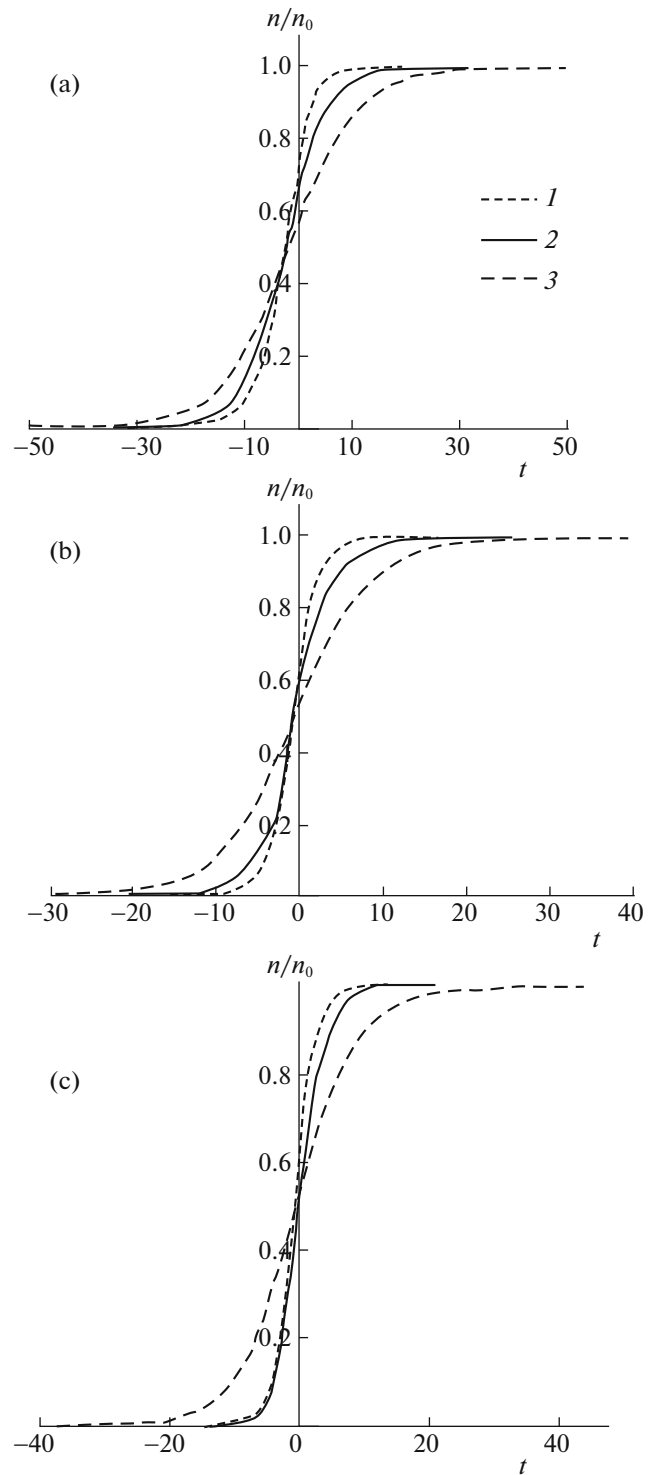

Fig. 2. Calculated elution curves of substances for sorption at three different values of the parameter at $\ln q = (1)$ −1, (2) 0, and (3) 1 at $\ln K = $ (a) 1, (b) 0, and (c) −1.

CONCLUSIONS

A model of the dynamics of the sorption of molecules was presented that considers characteristic features of transport in sorbents and the kinetic parame-

ter that determines the correlation between equilibrium concentrations of dissolved molecules in a solution and adsorbent. The effect of the correlation between the rates and characteristic times τ of the diffusion of impurity molecules in a liquid and solid body was demonstrated.

Analysis of the correlations between parameter K and the influence of solubility, and the difference between the energies of the interactions between the adsorbate and the solvent and adsorbent, demonstrated the role of the nature of the adsorbent and mobile phase in the sorption of adsorbates. We specified the conditions of the change in the width of the sorption front, depending on the size of grains and the concentration of impurity molecules in the liquid. The limiting cases of the kinetics of adsorption of impurity molecules from solutions were considered.

A number of conclusions can be drawn that are quite common and confirm the possibility of using the proposed model to describe the adsorption of substances.

1. When there are appreciable differences between the energies of interaction between the sorbate and the solvent (liquid) and adsorbent, and at fairly low concentrations of impurities in the liquid phase (low n), width λ of the front grows as the concentration of molecules falls upon relatively slow diffusion in the solid-phase medium ($K \ll p$ and n_0). This could correspond to when nonpolar solvents with a weak affinity toward the adsorbent (e.g., hexane and acetonitrile for silicas) are used as the mobile phase.

2. When there is a drop in temperature or an increase in solubility (n_0), the adsorption front shrinks exponentially and has a minimum width that is determined by the characteristic period of diffusion of molecules inside the grains.

The second group of conclusions largely demonstrates the advantages of ordered materials and their structure in describing the adsorption of organic molecules from solvents of different natures:

3. At fairly high values of $K \gg p$ and n_0 (with differences between the energies of interaction between the substance in the solution and the adsorbent, and with weak solubility of the adsorbate), the process that controls sorption from diffusion in a liquid to diffusion in a solid body can change, since K falls as the flow rate of the solution grows. At high K, width λ of the front grows along with the flow rate of the liquid solution and the size of the grains according to an exponential law. The asymmetry of the front also grows along with parameter p. This could correspond to when proton-donating and proton-accepting solvents with greater affinities toward the adsorbent (e.g., ethanol and ethyl acetate for silicas) are used.

4. An accurate solution that considers the equilibrium and kinetic parameters of sorption must be used in the transitional region of parameters where the mechanism controlling the process of adsorption changes from diffusion in grains to diffusion in liquids.

A formula for determining the characteristics of the sorption of substances in the formation and movement of a concentration front was thus obtained in this work. This analytical expression is true throughout the entire range of changes in the parameters determining the conditions of the occurrence of the process. Note that a substantial change in kinetic parameter K would be expected under conditions of the relatively fast diffusion of sorbates (including organic molecules) in the systems of ordered mesopores in the mesoporous analogs of MCM-41 and SBA-15.

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