Modeling and Experimental Chromatographic Measurements in Adsorption

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Abstract: - Reversed-flow inverse gas chromatography is extended to the experimental measurements of the probability density function for the adsorption energies as well as the differential energies of adsorption due to lateral interactions of molecules adsorbed on different heterogeneous solid surfaces. Thus, useful scientific information concerning the nature and the strength of the adsorbate-adsorbent and adsorbate-adsorbate interactions have been extracted in order to give appropriate answers to the questions: (a) Where are the molecules on the heterogeneous surface and (b) Which is the nature of the surface chemical bonds? The solids studied as adsorbents are the oxides of Calcium, Magnesium, Phosphorous and the adsorbates used hydrocarbons C_2 –C_4 as well as Ozone. The exponential stripping method of the PC program , used to calculate the necessary exponential coefficients of time is guided by the overall goodness of fit expressed by the square of correlation coefficient r^2. This coefficient is always in the range 0.990 - 0.999 showing a remarkable goodness of fit for a non-linear regression analysis. The programs also print, together with the exponential coefficients values, their standard errors, which were reasonable enough for physicochemical measurements.

Key-Words: - Reversed - Flow Gas Chromatography, Inverse Gas Chromatography, adsorption energies, probability density function for the adsorption energies, lateral interactions of molecules, adsorption on heterogeneous solid surfaces.

1 Introduction

The effect of adsorption heterogeneity and lateral interactions on adsorption phenomena and the role of different distributions of energetic sites have been studied and analyzed. For example, Hill employed a simple uniform distribution of energies to describe the heterogeneous surface and obtained an analytic expression for single gas adsorption.

Single and binary gas adsorption models are developed that account for surface heterogeneity as well as lateral interactions. The lateral interactions are of the Bragg-Williams type, a crude but simple approximation. A parametric study is carried out to investigate the effects of surface heterogeneity and attractive lateral interactions on single and binary gas adsorption isotherms [1].

On the other hand, adsorption isotherms and surface energy distribution functions on heterogeneous surfaces have been the subject of many efforts during the last two decades for characterizing heterogeneous solids by calculating adsorption energy distribution functions through retention volume data [2]. All these works offer approximate functions or values through approximate solutions without any determination of the actual values of adsorption parameters.

Of all the classical methods for measuring adsorption energies, isotherms etc none has led to local values. These methods lack the precision and the possibility of the Reversed Flow –Inverse Gas Chromatography RF-IGC method. Difficulties like these led scientists to turn into numerical solutions.

The RF-IGC is a simple and fast method for the determination of kinetic and energetic parameters, for the degradation diagnosis describing the action of one or two gases simultaneously on a solid surface. The RF-IGC method was used to measure directly from experimental data, not only kinetic physicochemical quantities, but also adsorption energies, local monolayer capacities, local adsorption isotherms, the probability density function for the adsorption energies as distributed over the experimental time [3,4]

The determination of the physicochemical quantities ε, c^*_{max}, θ_t and $\varphi(\varepsilon;t)$, [5-6] pertaining to heterogeneous surfaces, start from the diffusion band of RF-IGC experiments with the recording of the pairs H, t and the calculation of the pre-exponential factors A_1, A_2, A_3 and A_4, and the time

coefficients B_1, B_2, B_3 and B_4. By entering the pair values of H, t into the DATA lines of a non-linear regression analysis GW- PC program, together with the other unknown quantities in the INPUT lines, the required physicochemical parameters are calculated and printed [2, 4,5].

In some previous publications [7-11] a systematic presentation concerning the study of the interaction of gaseous hydrocarbons, with or without a second gas on different oxide surface has been done. The results obtained experimentally are in agreement with those coming through computer simulation studies for the system Ar / TiO$_2$ [12].

In this paper the chromatographic study is extended in order to investigate the kind of adsorption. The solids studied as adsorbents are the oxides of Calcium, Magnesium, Phosphorous and the adsorbates used hydrocarbons C_2 –C_4 as well as Ozone. Thus, through a time -resolved analysis the exact sorption phenomenon is studied easily and accurately and the chemisorption is well distinguished from the physisorption.

2 Experimental

The RF-IGC technique [3-4] involves a flow-rate perturbation of the carrier gas which is achieved experimentally simply by using a four- or six- port gas sampling valve and reversing the direction of flow of the carrier gas, usually for a short time interval. If pure carrier gas passes through the sampling column, nothing happens on reversing the flow. If a solute comes out of the diffusion column at z=0 (cf Fig.1) as the result of its diffusion into the carrier gas, filling the column z and also running along the sampling column, the flow reversal records the concentration of the solute at the junction of the sampling column with that of the diffusion one, at the moment of the reversal. This concentration recording has the form of extra chromatographic peaks superimposed on the otherwise continuous detector signal (cf Fig.2).

The experimental procedure includes the following stages:
a) Conditioning of each solid in situ at elevated temperatures for about 24 h with nitrogen flowing at the same flow rate.
b) Injection of 1 cm3 of each gas adsorbate at atmospheric pressure.
c) Measurement of the height of the sample peaks by reversing the direction of the carrier gas flow for an experimentally defined time which is a shorter time than the gas hold-up one. leave two blank lines between successive sections as here.
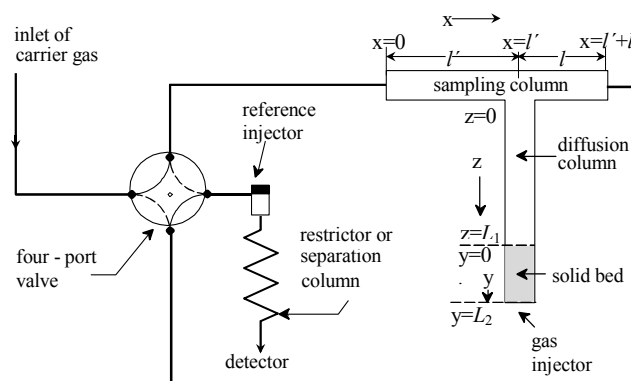

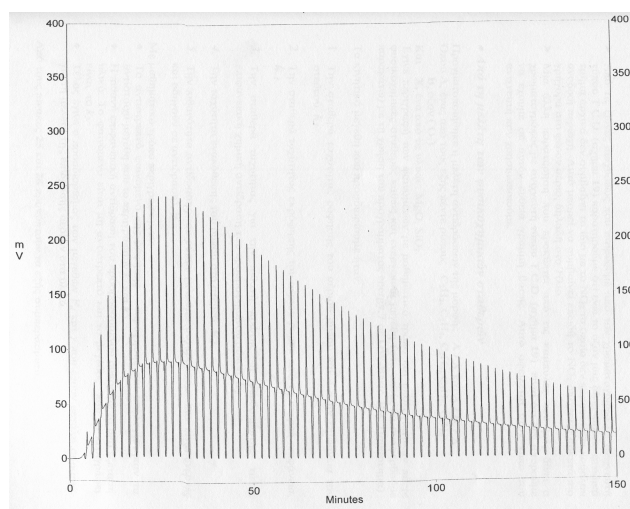Fig. 1, Schematic representation of the RF-IGC set-up for the study of adsorption parameters.

Fig.2 : Typical sample peaks obtained with the RF-IGC automatically.

2.1 Mathematical Model

The so-called diffusion band is obtained by plotting ln$H$ against t. Nothing can be gained by visual examination of such plots, but all adsorption quantities are calculated from these diffusion bands, by deriving an equation which describes them mathematically. This was based on the solution of a system of four partial differential equations, under given initial and boundary conditions. For this purpose, it is not necessary to determine the isotherm equation separately. Only the basic definition of the local adsorption equation is adopted, thus incorporating the real experimental isotherm in the mathematical calculations, any possible non-linearity is automatically taken care of.

A brief outline of the theory underlying adsorption parameters of gases on solids is given here. The main equation is Eq.(1)

$$H^{1/M} = gc(l',t) = \sum_{i=1}^{4} A_i \exp(B_i\, t) \qquad (1)$$

In Eq.(1) the symbols denote:
H, height of sample peaks resulting from the flow reversal, cm.
M, response factor of the detector, dimensionless.
g, calibration factor of the detector, cm / mol cm^{-3}
$c(l',t)$ measured sampling concentration of the analyte at $x = l'$ or $z = 0$, mol cm^{-3}.
The isotherms refer to the values of $c_y(0,t)$, i.e. the gaseous concentration of the analyte at $y = 0$:

$$c_y(0,t) = \frac{vL_1}{D_1} c(l',t) = \frac{vL_1}{gD_1} \sum_{i=1}^{4} A_i \exp(B_i\, t) \qquad (2)$$

where v is the linear velocity of the carrier gas (cm s^{-1}) in the sampling column and L_1 the length of the diffusion column (cm). From this, the value of the adsorbed concentration at equilibrium c^*_s is calculated:

$$c_s^* = \frac{\alpha_y}{\alpha_s} k_1 \frac{vL_1}{gD_z} \sum_{i=1}^{4} \frac{A_i}{B_i} [\exp(B_i t) - 1] \qquad (3)$$

and then the differential isotherm is found from the obvious relation:

$$\frac{\partial c_s^*}{\partial c_y} = \frac{a_y}{a_s} k_1 \frac{\sum_{i=1}^{4} A_i \exp(B_i t)}{\sum_{i=1}^{4} A_i B_i \exp(B_i t)} \qquad (4)$$

The local adsorption isotherm θ_t is found from relation

$$\theta_t = \frac{c_s^*}{c_{max}^*} \qquad (5)$$

where c^*_{max} is the local monolayer capacity
This concentration is given by the relation:

$$c_{max}^* = c_s^* + \frac{\partial c_s^*/\partial c_y}{KRT} \qquad (6)$$

where c^*_s is given by Eq.7 and the KRT by Eq.9:

$$K = K^0 \exp(\varepsilon / RT) \qquad (7)$$

$$K^0 = \frac{h^3}{(2\pi m)^{3/2}(kT)^{5/2}} \qquad (8)$$

$$KRT = \frac{gD_z}{vL_1} \left\{ \frac{\sum_{i=1}^{4} A_i B_i^2 \exp(B_i t)}{\left[\sum_{i=1}^{4} A_i B_i \exp(B_i t)\right]^2} - \frac{1}{\sum_{i=1}^{4} A_i \exp(B_i t)} \right\} \qquad (9)$$

The relations for calculating the adsorption energy ε (kJ/mol) and the modified probability density function $\varphi(\varepsilon)$ from experimental data are given by Eqs 10-13:

$$\varepsilon = RT \left[\ln(KRT) - \ln(RT) - \ln K^o \right] \qquad (10)$$

$$\varphi(\varepsilon;t) = \frac{\theta f(\varepsilon)}{c_{s\,max}^*} \qquad (11)$$

where

$$f(\varepsilon) = \frac{\partial c_{s\,max}^*}{\partial \varepsilon} = \frac{\partial c_{s\,max}^*/\partial t}{\partial \varepsilon/\partial t} \qquad (12)$$

The energy for the lateral interactions is given by Eq.13:

$$\beta = z\omega / RT \qquad (13)$$

where ω is the lateral interaction energy and z the number of neighbors for each adsorption site.

In all equations above A_i and B_i are the pre-exponential factors and the exponential coefficients of Eq.1. One can use τ in the above equations as a dummy independent variable for the time t and calculate, for chosen arbitrary values of τ, all three variables c_y, c^*_s and $\partial c^*_s/\partial c_y$. Plotting $\partial c^*_s/\partial c_y$ or c^*_s against c_y for each chosen τ, independent experimental isotherms can be obtained.

Starting with the experimental values H, t of the chromatogram of any system the required physicochemical quantities can be calculated by the suitable PC program [2-6] through the pre-exponential factors and the exponential coefficients of Eq.(1), namely the adsorption energy, the local adsorption isotherm, the local monolayer capacity, the energy distribution function, the dimensionless parameter β or $(\beta\theta)$ concerning lateral interactions, and the corresponding values of c_y all in relation to the experimental time.

The exponential stripping method of the PC program, used to calculate the exponential coefficients of time is guided by the overall goodness of fit expressed by the square of correlation coefficient r^2. This coefficient is always

in the range 0.990 - 0.999 showing a remarkable goodness of fit for a non-linear regression analysis. The programmes also print, together with the B values, their standard errors, which were reasonable enough for physicochemical measurements.

3   Results

With the use of suitable PC programs written in GW BASIC or FORTRAN, the study of the absorption∕ desorption phenomena of many adsorbates on different solids has become possible.

The RF-IGC method has the following advantages: (1) it is simple and fast; (2) it is accurate (3) the diffusion and resistance to mass transfer are taken into account while pressure gradient along the bed is negligible; (4) it leads directly to experimental isotherm without specifying an isotherm equation a priori; (5) the isotherm can be determined in the presence of a surface reaction of the adsorbate.

Beyond that, it creates a domain of time-resolved chemistry of surfaces, which provides experimental local values of adsorption energies, adsorption isotherms, monolayer capacities, probability density functions and lateral molecular interactions. Thus, all physicochemical quantities mentioned above can be determined as functions of experimental time by means of a simple PC program [2-6] and the plots can be provided through an Excel PC program [7-11]

From this point of view the RF-IGC method differs from the classical Chromatographic methods, being interested in the stationary phase properties rather than the solute ones. Thus, it provides information about the material surface nature and behavior in various environments, including individual material properties and air pollution influence on them. From an other point of view, traditional inverse gas –solid chromatography has about the same aims, but as it is a classical chromatographic elution method, it has several weak points: it does not take into account the sorption effect, it neglects the mass – transfer phenomena taking place, and also it is influenced by the carrier gas flow.

To give an answer to the question "where are located the adsorbed molecules on the surface", the topography of the active sites which is described from the variation of the energy distribution function over lateral energy values must be known. The positive values of β denote lateral attractions. The adsorption on the minima of potential energy is accompanied with repulsive forces, which decrease and become zero at monolayer surface coverage.

In all Figures (cf. Fig. 3) concerning the dependence of distribution function of adsorption energies from the experimental time one can distinguish between three types of adsorption active sites (groups A, B and C). As regards the time resolved analysis of lateral interactions a similar behavior as in the above case is observed [7-11]. On the other hand all Figures (cf. Fig.4) concerning the dependence of distribution function of adsorption energies from β experimental values one can distinguish between two types of adsorption active sites (only, groups B and C).
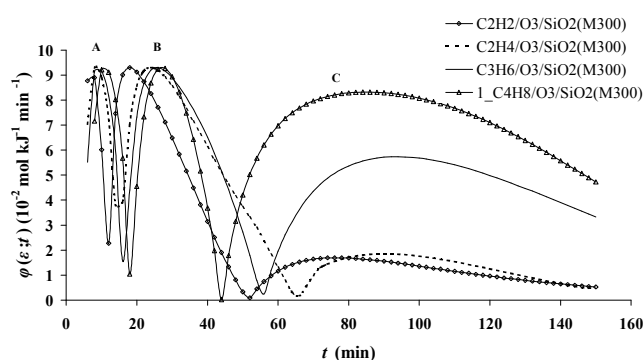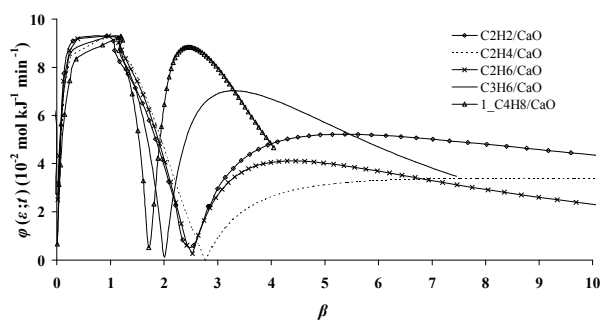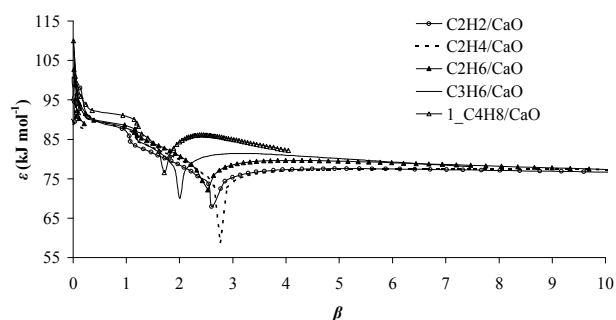

Fig.3, Density probability function, $\varphi(\varepsilon;t)$, versus time, t, for the systems: (a) $C_2H_2/O_3/SiO_2(M300)$, $C_2H_4/O_3/SiO_2(M300)$, $C_3H_6/O_3/SiO_2(M300)$, $1\_C_4H_8/O_3/SiO_2(M300)$, at 50°C.

Group A active sites indicate the chemisorption of the adsorbate on the minima of potential energy of the surface. The distribution of these active sites is random. These sites correspond to high values of coverage and adsorption energy. On the other hand, groups B and C of active sites correspond to adsorption at sites of lower energy and surface coverage. They are characterized by a patchwise topography. Adsorption sites in B are created through the lateral interactions with already adsorbed molecules, whereas, active sites in C are indicative of weak adsorption and island formation and are associated with a reconstruction of the surface compatible to chemisorption.

In order to have a correlation between the adsorbate-adsorbate interaction expressed by β and adsorbate-adsorbent interaction expressed by ε Figure 5 is given. It is obvious that when β increases ε diminishes. That is the chemisorption diminishes until a steady state for ε, while the Van der Waals forces increase. The same observation is valid from the θ-β (cf. Fig.6)
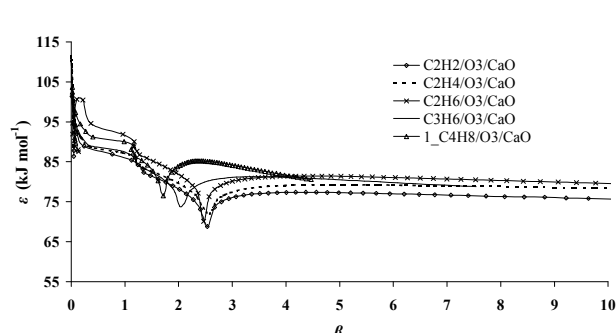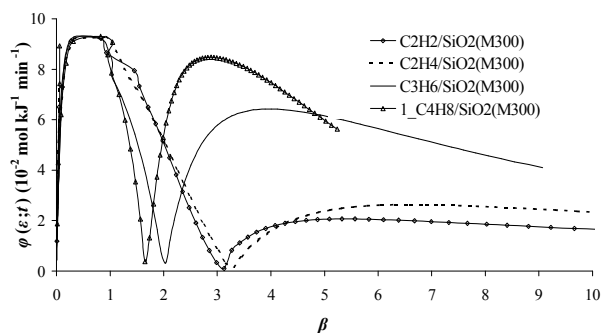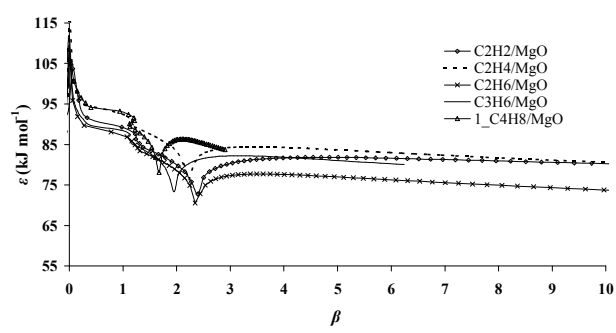
(a)

(b)
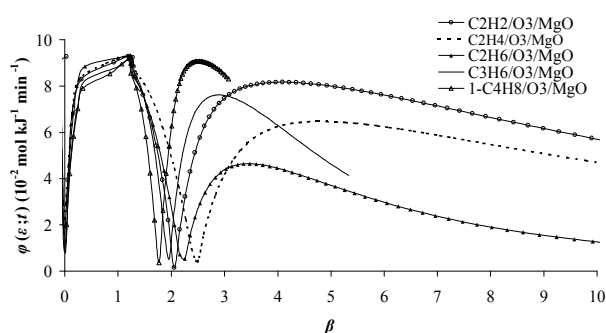
(c)

Fig.4, Density probability function, $\varphi(\varepsilon;t)$, versus energy for lateral interactions, β, for the systems: (a) C_2H_2/CaO, C_2H_4/CaO, C_2H_6/CaO, C_3H_6/CaO, $1\_C_4H_8/CaO$, (b) $C_2H_2/O_3/MgO$, $C_2H_4/O_3/MgO$, $C_2H_6/O_3/MgO$, $C_3H_6/O_3/MgO$, $1\text{-}C_4H_8/O_3/MgO$, (c) $C_2H_2/SiO_2(M300)$, $C_2H_4/SiO_2(M300)$, $C_3H_6/SiO_2(M300)$, $1\_C_4H_8/SiO_2(M300)$ at 50^oC, at 50^oC.

The physical meaning of high θ values is that there are stronger adsorbate-adsorbent interactions and random topography instead of active sites of lower θ values.

(a)

(b)

(c)

Fig.5, Adsorption energy, ε, versus energy for lateral interactions, β, for the systems: (a) C_2H_2/CaO, C_2H_4/CaO, C_2H_6/CaO, C_3H_6/CaO, $1\_C_4H_8/CaO$, (b) $C_2H_2/O_3/CaO$, $C_2H_4/O_3/CaO$, $C_2H_6/O_3/CaO$, $C_3H_6/O_3/CaO$, $1\_C_4H_8/O_3/CaO$, (c) C_2H_2/MgO, C_2H_4/MgO, C_2H_6/MgO, C_3H_6/MgO, $1\_C_4H_8/MgO$ at 50^oC.

All the above answer in detail the questions: (a) where are the molecules on the heterogeneous surface, (b) which is the nature of the surface chemical bonds.
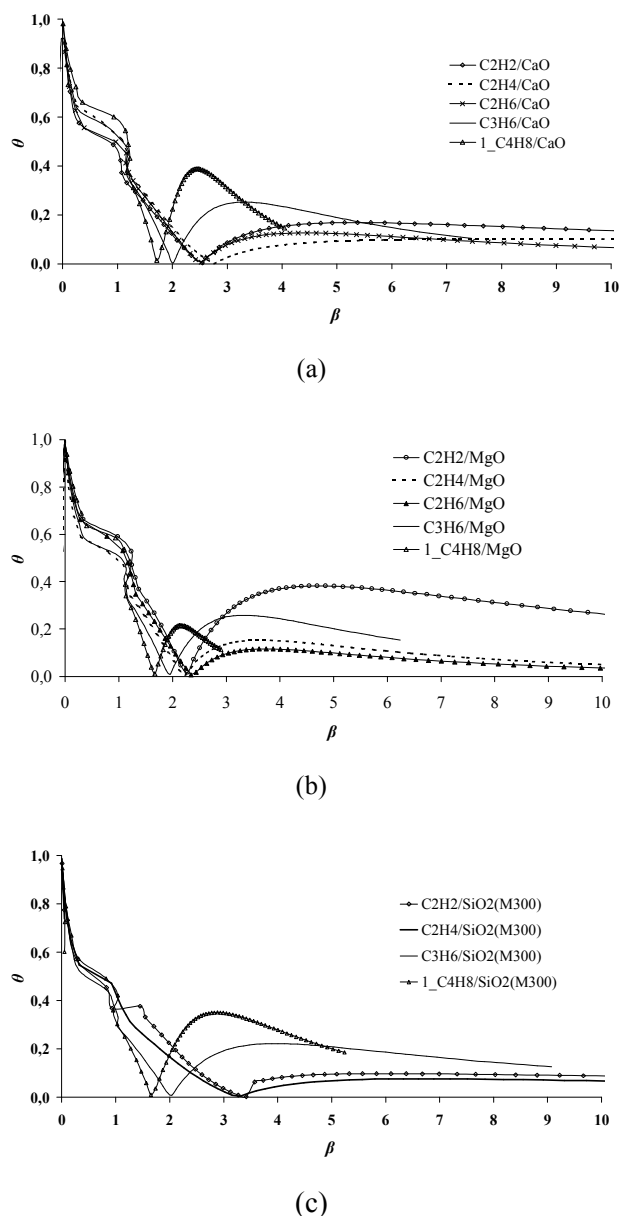
(a)

(b)

(c)

Fig.6, Local adsorption isotherm, θ, versus energy for lateral interactions, β, for the systems: (a) C_2H_2/CaO, C_2H_4/CaO, C_2H_6/CaO, C_3H_6/CaO, 1_C_4H_8/CaO, (b) C_2H_2/MgO, C_2H_4/MgO, C_2H_6/MgO, C_3H_6/MgO, 1_C_4H_8/MgO, (c) C_2H_2/ SiO_2(M300), C_2H_4/SiO_2(M300), C_3H_6/SiO_2(M300), 1_C_4H_8/SiO_2(M300) at 50°C.

Acknowledgment

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