

KINETIC AND THERMODYNAMIC EQUILIBRIUM OF ASPHALTENES SORPTION ONTO FORMATION ROCK: EVALUATION OF THE WASH IN THE ADSORPTIVE PROPERTIES

CINETICA Y EQUILIBRIO TERMODINAMICO DE LA SORCION DE ASFALTENOS EN ROCA: EVALUACIÓN DEL LAVADO EN LAS PROPIEDADES ADSORTIVAS

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ABSTRACT: The main objective was to obtain kinetic and thermodynamic equilibrium of asphaltene sorption onto powdered rock obtained from the Guadalupe formation (washed and unwashed) at different times, temperatures and concentrations. However, the effect of temperature in the equilibrium sorption was not significant. Rock powders were characterized by N₂ sorption at -196°C. Equilibrium sorption of asphaltenes in rock powders, within a range of concentrations from 250 to 1500 ppm, was determined using a static method. Sorption curves show Type I behavior, according to IUPAC. The Langmuir model was used for computing the monolayer asphaltene content values for the sorption at different temperatures, showing a good fit with respect to the experimental data. Sorption kinetics of asphaltenes in rock samples is a function of the concentration and for concentrations of 1500 ppm equilibrium is reached at about 90 min. Pseudo first order and pseudo second order kinetic models were applied to the experimental data for the different concentrations for the two rock samples, with a better result for the pseudo-first order kinetic model. The washing effect on the equilibrium was not significant; however the adsorptive capacity of the rock without washing was slightly higher than the rock washed with n-heptane and toluene.

KEYWORDS: Asphaltene, formation rock, sorption equilibrium, kinetic sorption.

RESUMEN: El principal objetivo del estudio fue obtener la cinética y el equilibrio termodinámico de la sorción de asfaltenos en polvo de roca obtenida de la formación Guadalupe (lavada y sin lavar), a diferentes tiempos, temperaturas y concentraciones. Sin embargo, el efecto de temperatura en el equilibrio de sorción no era significativo. Los polvos de roca fueron caracterizados por sorción de N₂ a -196°C. El equilibrio de sorción de los asfaltenos en los polvos de roca, dentro de un rango de concentraciones desde 250 hasta 1500 ppm, fue determinado usando un método estático. Las curvas de sorción muestran un comportamiento Tipo I, según la IUPAC. El modelo de Langmuir se usó para calcular los valores del contenido de asfaltenos monocapa para la sorción a diferentes temperaturas, mostrando un buen ajuste con respecto a los datos experimentales. La cinética de sorción de los asfaltenos en muestras de rocas es función de la concentración y para concentraciones de 1500 ppm el equilibrio es alcanzado alrededor de 90 min. Se aplicaron los modelos cinéticos de pseudo primer orden y pseudo segundo orden a los datos experimentales para las diferentes concentraciones para las dos muestras de rocas con un mejor resultado para el modelo cinético de pseudo-primer orden. El efecto de lavado en el equilibrio no fue significativo, sin embargo la capacidad adsorptiva de la roca sin lavar fue ligeramente mayor que la roca lavada con n-heptano y tolueno.

PALABRAS CLAVE: Asfalteno, roca, equilibrio de sorción, cinética de sorción.

1. INTRODUCTION

Asphaltenes are defined as the fraction of oil, bitumen or vacuum residue that is insoluble in low molecular weight paraffins such as n-heptane or n-pentane, while being soluble in light aromatic hydrocarbons such as toluene, pyridine or benzene [1,2]. The structure of asphaltenes is formed by polyaromatic cores attached to aliphatic chains containing heteroatoms such as nitrogen, oxygen, sulfur, and metals such as vanadium, iron and nickel [1-8]. Asphaltenes contain polar and non-polar groups (“amphiphilic” behavior) and tend to form colloidal aggregates. It has widely been documented that viscosity of heavy oils can dramatically increase by the asphaltene aggregation phenomenon [9,10].

Content of asphaltenes in a crude oil does not entail asphaltene related production problems. Most of the heavy oils with the greatest asphaltenes concentration are usually very stable during production, and asphaltenes do not promote well plugging on those wells. Quite the contrary asphaltene precipitation problems are more common in lighter crude oils that contain minor amounts of asphaltenes in sub-saturated reservoirs that are at pressures above bubble point. The potential for asphaltenes to plug systems as constituents of heavy oil is more visible downstream, forming rigid oil/water emulsions and creating organic fouling problems in refineries.

Several researchers have studied the adsorption of asphaltenes onto solid surfaces focused on understanding process phenomenology [11-21]. Gonzalez et al.[22] and Acevedo et al. [23] reported that the isotherms of asphaltene sorption onto mineral surfaces followed a Langmuir-type behavior, with a maximum adsorption capacity of 1-2 mg/m². Pernyeszi et al.[24] studied the effect of different types of materials (quartz, bentonite, clintonite and two cores taken at different well depths) on the asphaltene adsorption process. Authors found that isotherms showed a type I behavior according to the IUPAC criteria. Other works studying the adsorption of asphaltenes on adsorptive clays also concluded that isotherms exhibited a type I behavior, indicating the formation of a monolayer onto the porous matrix surfaces [25,26].

R. Z. Syunyaev, R. M. Balabin, I. S. Akhatov and J. O. Safieva [27], computed asphaltene adsorption parameters (maximum adsorption capacity, adsorption equilibrium constant and adsorption kinetic constants) for quartz, dolomite and mica sandstones, using Near Infrared Spectroscopy (NIRS). Adsorption data was a good fit to the Langmuir model. Mica sandstone presented greater adsorption capacity compared to other minerals.

Alkafeef, S. F. et al. [28] studied asphaltene adsorption onto porous rock surfaces. Adsorption data were obtained by electrokinetic potential measurements on several sandstone samples with asphaltenic oil. Langmuir’s isotherm was used as a theoretical approach to adsorption phenomenon.

Adsorption phenomena occur due to interactions between asphaltene aggregates and chemical compounds in minerals on rock surfaces. The governing forces in this behavior are electrostatic, charge transfer interaction, Van der Waals, steric repulsion and hydrogen bridge bonding [29-31].

Previous studies report that asphaltene and resin adsorption in aqueous and organic media onto clay minerals affect rock wettability, and decrease clay expansion, swelling and cationic exchange capacity. Adsorption phenomenon is deeply affected when an aqueous film is present in the medium[32].

José L. Mendoza de la Cruz et al.[20] studied asphaltene fraction adsorption from a Mexican oil dissolved in toluene on sandstone, limestone and dolomite rocks. For asphaltene concentrations lower than 6000 ppm, monolayer adsorption was observed. For higher concentrations, a multilayer adsorption was observed.

The aim of this work is to evaluate adsorption equilibrium of Guadalupe formation rock powder after being washed with n-heptane and toluene. So far, no asphaltene adsorption studies have been reported for asphaltenes extracted from Colombian oils.

2. EXPERIMENTAL

2.1. Materials

Asphaltenes were isolated from “The HOCHA” crude oil, which is heavy oil (19.2°API) produced from a

reservoir located in the south of Colombia. The rock powder was obtained from a sample extracted from Guadalupe Formation.

2.2 . Methods

2.2.1. Asphaltene isolation protocol

Asphaltene samples were isolated by following a standardized procedure. An excess of n-heptane (99% Sigma Aldrich) was added to the crude oil in a volume ratio of 40/L. The mixture was sonicated for 2 h at 25 °C and further stirred at 300 rpm for 20 h. The precipitated fraction was filtered using a 8 µm Whatman filter paper and washed with n-heptane at a ratio of 4/1 (g/mL). Asphaltene samples were centrifuged at 5000 rpm for 15 min and left to rest for 24 h. The cake was washed with n-heptane several times until the color of the asphaltenes became shiny black. Then, the sample was dried in a vacuum oven at 25 °C for 12 h. Finally, the obtained asphaltene was homogenized in a mortar [2]. Precipitated asphaltenes were dissolved in toluene to prepare a stock solution at 2000 mg/L. Solutions with different concentrations, 150, 250, 400, 750, 1000, 1500 and 2000 mg/L, were prepared from the stock solution.

2.2.2. Rock powder obtention and washing

From the rock sample belonging to the Guadalupe formation, 9g of rock powder was milled. Half of the powder obtained was washed with 10ml toluene and n-heptane for each gram of powder, and then the sample was filtered until the discarded toluene was colorless. The other half was used without any treatment.

2.2.3. Samples characterization

The powder samples were characterized by N₂ adsorption at -196°C. Nitrogen adsorption isotherms were obtained with an Autosorb-1 from Quantacrome after outgassing samples overnight at 140 °C under high vacuum (10⁻⁶mbar). BET surface area (S_{BET}) values were calculated using the model of Brunauer, Emmet and Teller (BET) presented by Rouquerol et al. [33].

2.2.4. Adsorption experiments

A calibration curve of UV absorbance versus asphaltene concentration at 400 nm was

constructed from the prepared solutions with known concentrations. Toluene was used as a solvent agent for dilution, as well as the blank in the calibration curve construction [4,34].

A constant mass of the rock powder sample (100 mg) was added to the asphaltene solutions of constant volume (10 mL). Each solution was stirred at 200rpm for 10 h at 25, 40, 55 and 70 °C in order to reach the sorption equilibrium. The time evolution of the measured asphaltene concentration indicated that a time of 1 h was enough to reach the sorption thermodynamic equilibrium. When asphaltene solutions with high concentrations (greater than 250 mg/L) were tested, an additional dilution with toluene was necessary in order to obtain the desired absorbance value within the calibration curve.

3. MODEL

3.1. Kinetic model

In order to predict the rate at which asphaltenes adsorb onto rock surfaces, two adsorption kinetic models, pseudo-first-order and pseudo-second-order, have been used. The pseudo-first-order kinetic model is expressed in [35] as:

$$\frac{dN_{ads}}{dt} = k_1 (N_{ads,eq} - N_{ads}) \quad (1)$$

where $N_{ads,eq}$ (mg/g) and N_{ads} (mg/g) are the amounts of adsorbed asphaltene on rock powder at equilibrium and at time t , respectively, and K_1 (h) is the kinetic constant of pseudo-first-order adsorption. The model is expressed in a linear form to plot the experimental data, in order to obtain the slope and intercept and determine $N_{ads,eq}$ and K_1 .

The pseudo-second-order kinetic model is expressed in [36,37] as:

$$\frac{dN_{ads}}{dt} = k_2 (N_{ads,eq} - N_{ads})^2 \quad (2)$$

The second order kinetic constant k_2 (h) and the amount of asphaltenes adsorbed at the equilibrium $N_{ads,eq}$.

(mg/g) are obtained from the slope and intercept of the

experimental data plot, fitted to the linear form of the model.

3.2. Langmuir Model

The Langmuir model has been widely used to correlate experimental data of equilibrium sorption [38]. This model assumes that the process occurs on a homogeneous surface by monolayer adsorption. It was originally derived from kinetic data of adsorption and desorption, taking into account that equilibrium is obtained when the rates of adsorption and desorption are equal. The Langmuir equation can be expressed as follows:

$$N_{ads} = N_{ads,max} \left(\frac{K_L C_E}{1 + K_L C_E} \right) \quad (3)$$

where N_{ads} is the amount of asphaltenes adsorbed onto rock powder (mg/g), C_E is the equilibrium concentration of asphaltenes in the solution phase (mg/L), K_L is the Langmuir equilibrium adsorption constant related to the affinity of binding sites (L/mg), and is defined as the monolayer saturation capacity, $N_{ads,max}$ representing the maximum amount of asphaltenes per unit mass of nanoparticles for complete monolayer coverage (mg/g).

3.3. Thermodynamic properties

The thermodynamic properties were calculated in order to characterize the adsorption phenomenon and process spontaneity. They were estimated from the classical expression for the Gibbs free energy change ΔG_{ads}^o [KJ/mol][4]:

$$\Delta G_{ads}^o = RT \ln K \quad (4)$$

where R is the universal constant for ideal gases, T is the absolute temperature, and K is the adsorption equilibrium constant. K is related to the energy of adsorption and can be expressed as $K_L C_s$, where C_s is the solvent molar concentration. The changes of sorption enthalpy (ΔH_{ads}^o [KJ/mol]) and entropy (ΔS_{ads}^o [KJ/K.mol]) were calculated from the plot of ΔG_{ads}^o versus temperature [39].

$$\Delta G_{ads}^o = \Delta H_{ads}^o - T \Delta S_{ads}^o \quad (5)$$

To determine the Langmuir constant it is necessary to know the molecular weight of the asphaltene. However, due to its dependence on the chemical nature of the crude oil from which asphaltenes were isolated, and the intrinsic complexity of the asphaltene structure, this property is still an unsolved issue [17]. For this reason, thermodynamic properties were calculated taking into account the extremes of the typical range of molecular weight of asphaltenes reported in the literature (750-5000 g/mol) [2].

4. RESULTS AND DISCUSSION

4.1. Sorption isotherm of asphaltene

The rock powder has 15 m²/g of external surface area. Sorption isotherms of asphaltene onto washed sample and unwashed samples at 25°C are shown in Figure 1, where the unwashed sample shows a higher adsorptive capacity than the other sample. This phenomenon might have happened because during washing, some components present in the rock surface with affinity towards asphaltenes were removed. However, the difference between the adsorption capacities is not remarkable.

For the same concentration, in this case, 860 mg/L, the adsorptive capacity for the unwashed sample was 14.17 mg/g, while for the washed sample was 13.31 mg/g, 9% less than the unwashed sample. According to this result, the adsorption response in both samples is very similar.

Type I behavior was observed in the sorption isotherms of asphaltenes onto rock powder. These results are in agreement with Jose L. Mendoza de la Cruz [20], who studied the asphaltene adsorption onto sandstone, limestone and dolomite.

The Langmuir model was used for analyzing the asphaltene adsorption isotherms. The model parameters calculated for the isotherms of asphaltene adsorption on rock powder samples are presented in Table 1. As indicated by the values of the regression coefficients, the experimental data were adequately described by the model, presenting a Type I behavior [2]. For each rock powder sample, the asphaltene content of the monolayer ($N_{ads,max}$), calculated by linear regression,

was equal for all adsorption temperatures. Figure 2 shows isotherms behavior for the asphaltene sorption

onto the washed sample (a) and the unwashed sample (b) at 25, 40, 55 and 70°C.

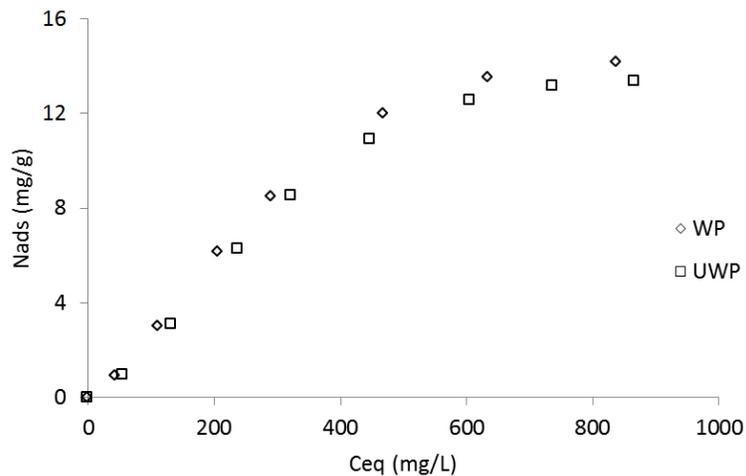


Figure 1. Asphaltene sorption isotherms onto washed rock powder (WP) and unwashed rock powder (UWP)

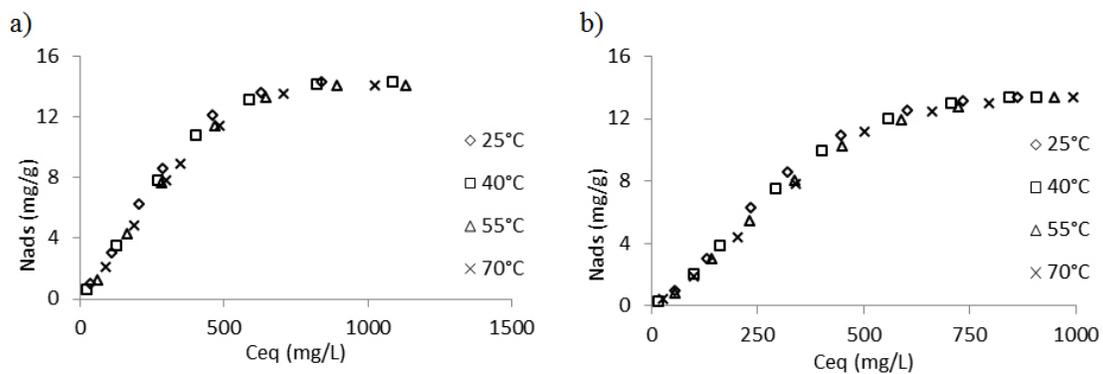


Figure 2. (a) Sorption isotherms of asphaltenes onto washed rock at 25, 40, 55 and 70°C. (b) Sorption isotherms of asphaltenes onto unwashed rock at 25, 40, 55 and 70°C.

The Langmuir model had correlation coefficients of 0.92 for de washed sample and 0.96 for the unwashed sample. There was a slight difference between the experimental data and the values obtained with the model mainly for high concentrations.

4.2. Thermodynamics properties of asphaltene sorption

The calculated thermodynamic parameters for the sorption of asphaltenes on the washed and unwashed samples are given in Table 2. The change in the free Gibbs energy (ΔG_{ads}^o) was inversely proportional to temperature. A negative value of ΔG_{ads}^o indicates the status of feasibility and spontaneity of thermodynamic

processes, i.e., it characterizes the natural tendency of a system to undergo spontaneous changes [33,38]. The ΔG_{ads}^o values obtained were in agreement with those reported by Nassar [2]. The negative value of ΔH_{ads}^o suggests the exothermic nature of the sorption process. This is in agreement with the finding that the adsorption is rapid and decreases with the temperature [2].

4.3. Sorption Kinetics of asphaltene

To determine kinetic parameters, the amount of asphaltenes adsorbed was calculated from concentration measurements at different times, for 250, 750 and 1500 mg/L, as shown in Figure 3 and Figure 4 for unwashed and washed samples

respectively. The results indicate that equilibrium is reached faster for lower initial concentration (30 min for 250 mg/L; 70 min for 750 and 1500 mg/L). Kinetic constants (k_1 and k_2) and amounts of adsorbed asphaltene at the equilibrium ($N_{ads,eq}$) obtained are summarized in Table 3. Furthermore,

experimental data fitted better to pseudo-first-order model, (Table 3.) which suggests that adsorption of asphaltene onto rock powder follows a first order kinetic. Finally, values obtained with kinetic models of pseudo-first order are in agreement with experimental data obtained in this study as shown in Table 3.

Table 1. Asphaltene sorption isotherms onto washed rock powder (WP) and unwashed rock powder (UWP)

Material	$N_{ads,max}$ (mg/g)	K_L (L/mg)	R^2
Unwashed rock Powder	17.67	0.003	0.96
Washed rock Powder	26.45	0.001	0.92

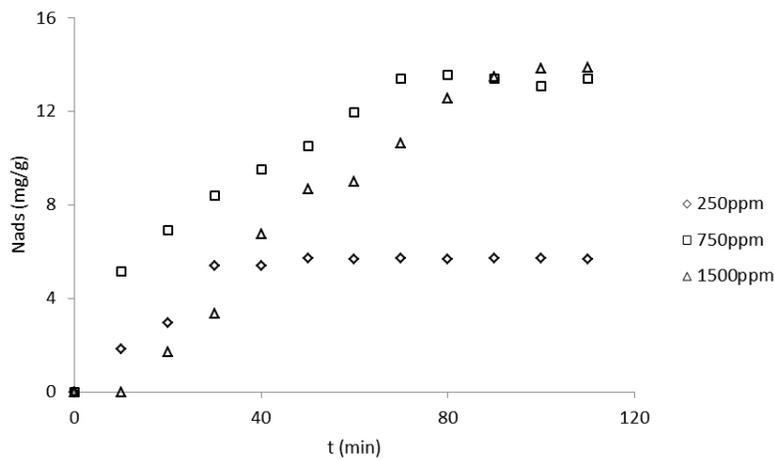


Figure 3. Amount of asphaltene adsorbed on unwashed rock powder versus time for different initial concentration of asphaltenes at 25°C.

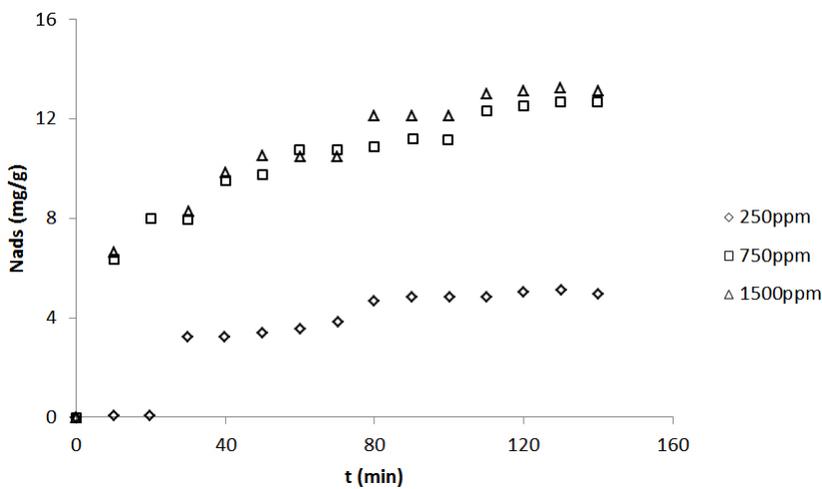


Figure 4. Amount of asphaltene adsorbed on washed rock powder versus time for different initial concentration of asphaltenes at 25°C.

Table 2. Calculated values of ΔG_{ads}^o , ΔH_{ads}^o and ΔS_{ads}^o for asphaltene adsorption on washed and unwashed rock

Material	Asphaltenes molar mass (g/mol)	Temperature (K)	<i>K</i>	$-\Delta G_{ads}^o$ (kJ/mol)	$-\Delta H_{ads}^o$ (kJ/mol)	$-\Delta S_{ads}^o$ (J/mol-K)	R ²
Unwashed rock Powder	5000	298.18	144767.45	29.45	2.66	89.87	0.99
		313.16	137813.69	30.81			
		328.16	131497.34	32.16			
		343.16	125734.61	33.49			
	750	298.18	21715.90	24.75	2.66	74.10	0.99
		313.16	20672.05	25.87			
		328.16	19794.60	24.51			
		343.16	18860.19	24.40			
Washed rock Powder	5000	298.18	59680.82	27.26	2.66	82.50	0.99
		313.16	56814.69	28.50			
		328.16	54210.53	29.73			
		343.16	51834.96	30.97			
	750	298.18	8952.12	22.56	2.66	66.73	0.99
		313.16	8522.15	23.56			
		328.16	8131.58	22.31			
		343.16	7775.24	22.20			

Table 3. Kinetic model parameters for the asphaltene adsorption onto washed and unwashed rock powder at 25°C

Initial concentration (mg/L)	<i>N_{ads,eq}</i> experimental (mg/g)	Pseudo First order			Pseudo Second order			
		<i>N_{ads,eq}</i> (mg/g)	<i>k₁</i> (h ⁻¹)	R ²	<i>N_{ads,eq}</i> (mg/g)	<i>k₁</i> (h ⁻¹)	R ²	
Unwashed rock Powder	250	5.70	5.50	2.07	1.00	6.89	0.49	0.96
	750	13.58	12.51	1.85	0.96	17.33	0.12	0.98
	1500	13.88	18.75	1.40	0.96	39.68	0.01	0.71
Washed rock Powder	250	4.80	4.82	1.48	0.94	1.20	16.18	0.96
	750	12.31	7.01	1.17	0.98	1.27	22.67	0.98
	1500	12.98	7.76	1.06	0.98	2.20	3.04	0.79

CONCLUSIONS

The asphaltene sorption isotherms of rocks (washed and unwashed) at 4 temperatures (25, 40, 55 and 70°C) and different concentration levels were determined using the static method. The equilibrium asphaltene content slightly increased with decreases in temperature at a constant asphaltene concentration. Additionally, the temperature dependence of sorption isotherms could be predicted with reasonable accuracy with Langmuir model. However, the temperature effect is not significant.

The monolayer moisture content values for desorption at different temperatures were determined using a Langmuir model. However, the temperature effect is

not significant. Superior results were obtained when the washed powder rock.

The thermodynamics properties of asphaltene adsorption on rocks reaffirm the spontaneity and exothermic nature of the adsorption process. Equilibrium constants, adsorption capacities, and thermodynamic parameters for asphaltene adsorption onto rocks were computed and compared with the literature, which is agreement.

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