

ADSORPTION ISOTHERMS OF PHENOL AND 4-CHLOROPHENOL ON PETROLEUM ASPHALTENES

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ADSORPTION DU PHÉNOL ET DU 4-CHLOROPHÉNOL SUR LES ASPHALTÈNES PÉTROLIERS

Les isothermes d'adsorption du phénol et du 4-chlorophénol en solution dans l'eau sur des asphaltènes floculés en masse et sur des asphaltènes déposés sur de la silice ont été déterminés par analyse chromatographique frontale à 293, 298, 303 et 308 K. L'adsorption sur des asphaltènes floculés en masse était la plus importante avec des isothermes correspondant à un mécanisme de Freundlich. La quantité élevée de phénols adsorbés suggère une migration possible des molécules du phénol à travers la structure peu compacte des asphaltènes. Les isothermes observés dans le cas de silice tapissée d'asphaltènes ont montré que l'adsorption se produit en deux étapes correspondant probablement à deux organisations différentes des molécules de soluté à la surface.

ADSORPTION ISOTHERMS OF PHENOL AND 4-CHLOROPHENOL ON PETROLEUM ASPHALTENES

The adsorption isotherms for phenol and 4-chlorophenol from water onto asphaltenes flocculated in bulk and asphaltenes deposited on silica were established by frontal analysis chromatography at 293, 298, 303, and 308 K. The adsorption was more important with asphaltenes flocculated in bulk and corresponded to a Freundlich isotherm mechanism. The high adsorbed amount of phenols suggests possible migration of phenols through the loose asphaltene structure. Isotherms observed with the silica coated by asphaltenes showed that adsorption occurs in two stages corresponding probably to two different organizations of solute molecules at the surface.

ADSORCIÓN DEL FENOL Y DEL 4-CLOROFENOL EN LOS ASFALTENOS PETROLEROS

Los isoterms de adsorción del fenol y del 4-clorofenol en solución en el agua respecto a los asfaltenos floculados en masa y, asimismo, en los asfaltenos depositados sobre sílice, se han determinado por análisis cromatográfico frontal a 293, 298, 303 y 308 K. La adsorción en los asfaltenos floculados en masa fue la más importante con los isoterms correspondientes a un mecanismo de Freundlich. La elevada proporción de fenoles adsorbidos viene a sugerir una posible migración de las moléculas del fenol a través de la estructura poco compacta de los

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asfaltenos. Los isoterms observados en el caso de sílice recubierta de asfaltenos han permitido demostrar que la adsorción tiene lugar en dos etapas que corresponde, probablemente, a dos organizaciones diferentes de las moléculas de la solución en la superficie.

INTRODUCTION

Interactions of phenol with asphaltenes were used by Barbour and Patersen (1974) to characterize a density of basic sites of asphaltenes. In the present work this approach was used to investigate differences of adsorbing properties of asphaltenes flocculated in bulk or deposited on a solid surface (silica grains). The frontal analysis chromatography was used to measure the adsorption isotherms in both cases. This technique was often used in the literature for this purpose. Recently, Akgerman and Zardkoohi (1996) studied the adsorption of phenolic compounds on fly ash. Juang *et al.* (1996) had established the adsorption isotherms of phenols onto activated carbon fibers at 303 K. The results obtained by frontal analysis chromatography compare generally well with batch measurements.

1 EXPERIMENTAL SECTION

1.1 Materials

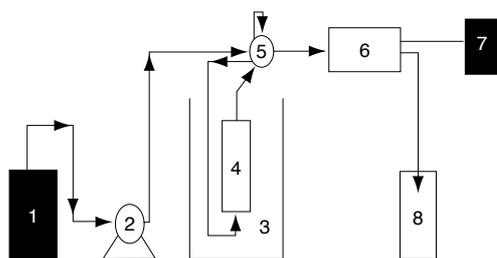
The asphaltenes used in this study were obtained from asphalts deposited from the crude oil and furnished by the *Institut français du pétrole*. According to the NFT 60-115 norm, the asphalt samples (20 g) were ground before extraction and next extracted with heptane. Then the precipitate was filtered and extracted with toluene. The asphaltene granulometry was measured using standard sieves according to the NFX 11-504 norm. The asphaltene particle size selected for this work was in the range 0.2-0.62 mm.

The phenolic compounds purchased from *Aldrich Chemical Co.* were of purity higher than 99%. They were used without any further purification.

Deionized water used for solution preparation had a conductivity of about 1-1.8 $\mu\text{S}/\text{cm}$. The corresponding pH was 5.6.

1.2 Procedure

The apparatus is shown in Figure 1. Measurements were performed with a chromatographic system equipped with a Shimadzu LC-6A metering pump, a Iota refractive index detector, a Rheodyne switching valve, a 5 cm long column, and a computer for data acquisition. The column was immersed in a bath the temperature of which was maintained constant to



- | | |
|-----------------------------|-----------------------------|
| 1 Mobile phase reservoir | 5 Switching valve |
| 2 Metering pump | 6 Refractive index detector |
| 3 Constant temperature bath | 7 Data acquisition |
| 4 Column | 8 Waste reservoir |

Figure 1
Expérimental apparatus based on frontal analysis chromatography

within ± 0.1 deg by a Lauda RM6 thermostat. The mobile phase was an aqueous phenolic solution of known concentration.

The column was filled with a stationary phase, i.e. asphaltenes flocculated in bulk or asphaltenes deposited on silica. In the second case, silica grains (Mesh Chromosorb 60-80 WAW-DMCS from *Supelco*) were impregnated with 15% asphaltenes by mixing 2.843 g of silica and 0.458 g of asphaltenes in a 10 ml volume of tetrahydrofuran. The solvent was evaporated during three hours at 323 K, using a rotary evaporator working at minimum rotor speed in view to obtain a homogeneous asphaltene layer at the silica surface.

The porosity ε of the stationary phase was measured by high performance liquid chromatography in the following way:

$$\varepsilon = \frac{V_M}{V_C} \quad (1)$$

where V_C is the column volume and V_M the dead volume. Dead volume V_M was determined injecting a solute not adsorbing on the stationary phase. In the case the choice of a non-adsorbing solute is not evident. After preliminary tests it was found that acetone has the shortest retention time. Therefore it was used to determine the dead volume. The values of porosity found were 0.43 and 0.69 respectively for asphaltenes flocculated in bulk and for silica coated with asphaltenes.

To obtain adsorption isotherms of the phenolics (phenol, 4-chlorophenol), five solutions of concentrations in the range 10-90% of the solubility limit of

the phenolic compound in water were prepared. The aqueous solubilities are given in Table 1 as a function of temperature. They were obtained by conductivity measurements (Achar *et al.*, 1996). Each solution was filtered (pores of 0.45 μm diameter) and degassed with helium prior being used in frontal analysis chromatography.

TABLE 1

Solubilities of phenolics at different temperatures (Achar *et al.*, 1996)

Compound	$t/^\circ\text{C}$	$S/(\text{g L}^{-1})$
Phenol	15.1	76.044 ± 0.014
	25.0	84.045 ± 0.011
	35.0	93.098 ± 0.029
4-chlorophenol	15.1	23.337 ± 0.017
	25.2	25.540 ± 0.020
	34.6	28.499 ± 0.053

At the start of each experiment, the asphaltene column was bypassed and a steady state voltage output from the refractive index detector for each of the five different organic concentrations was recorded. This enabled us to determine a calibration curve which was later used to convert voltage to concentration prior to data processing and establishing of adsorption isotherms. The calibration coefficient p_{cf} was found from the following linear expression:

$$C = p_{cf} V \quad (2)$$

where C and V are respectively the solute concentration and the voltage delivered by the detector. The calibration curves were established for phenol and 4-chlorophenol at 293, 298, 303 and 308 K. They were linear with R^2 values of > 0.99 . The calibration coefficients p_{cf} are given in Table 2.

TABLE 2

Calibration coefficients p_{cf} for frontal analysis chromatography

T/K	Phenol	4-chlorophenol
293	21.08	39.70
298	20.07	27.83
303	19.18	19.58
308	18.86	13.51

When the stability of the voltage reading was obtained, the phenolic solution was switched on the column, and the response of the detector versus time

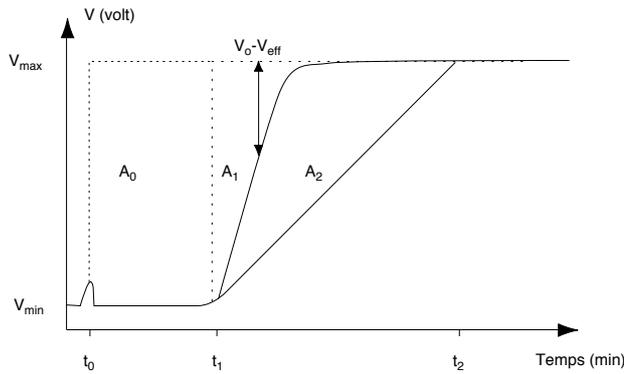


Figure 2

A typical breakthrough curve for adsorption of phenol on asphaltenes

was measured and stored. The calibration curve was used to convert the voltage to concentration. Figure 2 shows a typical breakthrough curve for adsorption of phenol on an asphaltene sample. Each adsorption experiment was terminated when the effluent concentration from the column reached a steady state value equal to the inlet concentration. The mass of solute accumulated in the column during the adsorption process is given by a mass balance:

$$m_{accumulated} = m_{in} - m_{out} \quad (3)$$

where m_{in} and m_{out} are the inlet and outlet mass flow rates given respectively by:

$$m_{in} = \int_0^t v(t) C_o dt \quad (4)$$

and

$$m_{out} = \int_0^t v(t) C_{eff} dt \quad (5)$$

$v(t)$ is the volumetric flow rate (0.4-0.5 cm³/min in this work) and C_o and C_{eff} are the concentrations of the inlet stream and of the effluent respectively. It can be observed that C_{eff} is not a constant in time; it changes from nearly zero at the beginning to C_o at the end of experiment. The mass accumulated in the column is then given by:

$$m_{accum.} = \int_0^t [C_o - C_{eff}] v(t) dt \quad (6)$$

The flow rate, $v(t)$, can be assumed to be constant and equal to the water feed rate to the column.

Using Equation 2 to convert concentrations to voltage values, we obtain:

$$m_{accum.} = v(t) p_{cf} \int_0^t [V_o - V_{eff}] dt \quad (7)$$

The integral term in Equation 7 corresponds to the area $A_0 + A_1$ on Figure 2. The analysis of the breakthrough curve yields a point on the adsorption isotherm.

Moreover, a part of the solute accumulated in the column is not adsorbed at the surface of grains, but simply retained in the space between grains. To account for this column void space, the porosity ϵ is introduced and the amount adsorbed on asphaltenes is:

$$m_{ads} = m_{accum.} - C_o v_o \epsilon \quad (8)$$

where v_o corresponds to the mobile phase volume passed through the column during experiment.

2 RESULTS AND DISCUSSION

Adsorption isotherms of phenol and 4-chlorophenol have been established at four different temperatures: 293, 298, 303 and 308 K. The results obtained with asphaltenes and asphaltenes deposited on silica grains are given in Figures 3-6. In overall systems, an increase in temperature favors the desorption of the solute.

In the case of asphaltenes flocculated in bulk, the isotherms can be characterized by a convex Freundlich isotherm (i.e., $n < 1$) indicating that no significant adsorption takes place at low concentrations. At higher concentrations, interactions between solute and asphaltenes turn to be stronger and adsorption becomes significant. The cooperative adsorption of phenolic compounds has been described for silica and alumina (Giles *et al.*, 1960). It may be attributed to physico-chemical properties of the adsorbates. Phenols have a strong hydroxyl functional group that interacts with the adsorbent surface, resulting in vertical alignment of the molecule on the surface. Moreover, additional adsorption is motivated and consequently the interaction between the adsorbed molecules. This phenomenon is known to contribute significantly to the cooperative nature of adsorption and hence a S type curve. At a 0.2 mol/l solute equilibrium

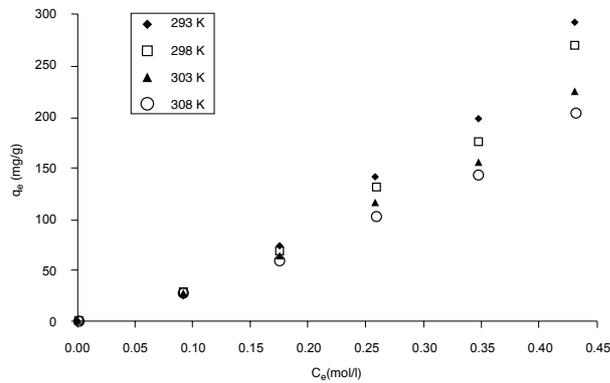


Figure 3
Adsorption isotherms of phenol on asphaltenes flocculated in bulk at different temperatures.

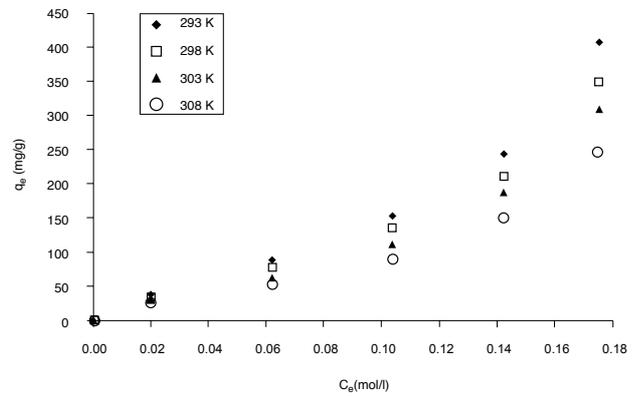


Figure 4
Adsorption isotherms of 4-chlorophenol on asphaltenes flocculated in bulk at different temperature.

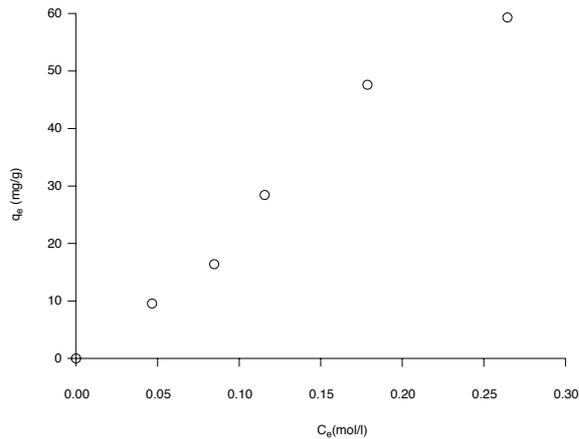


Figure 5
Adsorption isotherms of phenol on coated asphaltenes at 308 K.

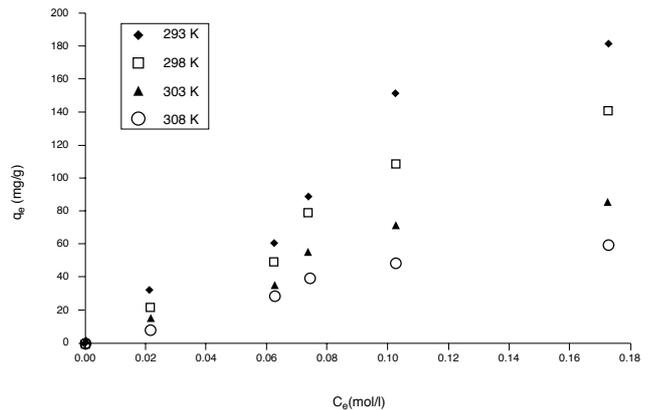


Figure 6
Adsorption isotherms of 4-chlorophenol on coated asphaltenes at different temperatures.

concentration, asphaltenes adsorb 70 and 450 mg/g for phenol and 4-chlorophenol, respectively. The affinity of chlorinated phenol for asphaltenes is very high compared to phenol.

Adsorption isotherms obtained with coated asphaltenes cannot be characterized by a Freundlich isotherm. Two steps can be clearly observed in the adsorption process. The limit between these two steps is observed at solute concentrations of about 0.1 mol/l. This change in the shape of isotherm is probably due to a modification of the molecular organization of phenol or 4-chlorophenol at the silica surface. As previously observed with asphaltenes flocculated in bulk, the

4-chlorophenol is more adsorbed than phenol. At a 0.2 mol/l solute equilibrium concentration, the amount of adsorbed 4-chlorophenol is near 200 mg/g against 40 mg/g for phenol.

Comparing the amounts of solute adsorbed per gram of adsorbent in both cases (asphaltenes and coated asphaltenes), one may notice that q_e is significantly higher in the case of asphaltenes flocculated in bulk. These results suggest the possible migration (absorption) of phenolic compounds through the loose asphaltene structure. Asphaltenes deposited on silica have probably a more compact organization resulting in a negligible migration.

In conclusion, equilibrium studies were carried out to characterize interactions of phenols with asphaltenes. High adsorption capacities (about 3.5 mol/kg with asphaltenes flocculated in bulk) were obtained for chlorinated phenol compared to other adsorbents such as fly ash (less than 1 mol/kg) or activated carbon fibers (about 2 mol/kg).

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