



## Adsorption of asphaltenes on kaolinite as an irreversible process



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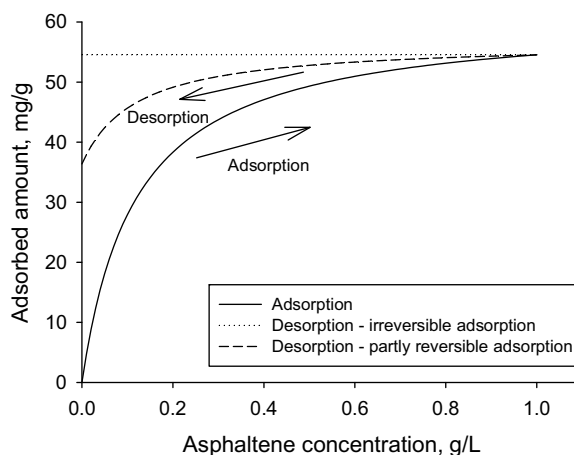
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### HIGHLIGHTS

- Experiments with different initial conditions demonstrate that equilibrium isotherms do not apply to asphaltene adsorption.
- First examination of irreversible adsorption as a kinetically limited deposition analogous to other colloids such as proteins and polymers.
- Define the surface coverage of the minerals and the desorption of the asphaltenes in terms of irreversible adsorption processes.

### GRAPHICAL ABSTRACT

Adsorption of asphaltenes with increasing solution concentration (adsorption), then decreasing concentration (desorption) with and without irreversible interaction with the surface.



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### ABSTRACT

The adsorption of asphaltenes on mineral surfaces is important in petroleum production and in oilsands extraction. Adsorption of Athabasca asphaltenes from toluene solutions onto kaolinite was investigated over a wide range of asphaltene and kaolinite concentrations. Although the adsorption appeared to follow the functional form of the Langmuir isotherm, the amount adsorbed depended on the kaolinite concentration so that the result depended on the experimental path, not the final solution concentration of asphaltenes. The results are consistent with kinetically limited adsorption, analogous to proteins, with a functional dependence on the asphaltene/kaolinite ratio. Multiple contacts between dried asphaltene-coated kaolinite and fresh asphaltene solutions, and between “spent” asphaltene solutions and fresh samples of kaolinite further confirmed that conventional isotherms were inadequate to describe the adsorption behavior. Repeated contact of asphaltene solution with kaolinite adsorbed up to 98% of the asphaltenes, therefore, the adsorption was not selective for specific species in the asphaltene mixture. Kaolinite samples before and after multiple contacts with asphaltene were analyzed by elemental analysis and X-ray photoelectron spectroscopy (XPS). The adsorption density of asphaltene on kaolinite increased dramatically after each contact with a fresh asphaltene solution, but the surface composition detected by XPS on the kaolinite surface was unchanged. The presence of Al and Si, detectable even at high asphaltene

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adsorption density, proved that asphaltene adsorption layer is not continuous on the kaolinite surface, and that subsequent asphaltene adsorption occurred preferentially on the asphaltenes already adsorbed on the kaolinite surface.

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## 1. Introduction

As the heaviest and most polar component in petroleum, asphaltenes are composed of condensed aromatic rings attached to alkyl chains, bridges, and naphthenic rings. Rich on polar groups, the asphaltenes tend to associate and aggregate to form various sizes of colloidal particles depending on temperature, pressure and concentration [1–3]. Some of these particles are surface active and are able to stabilize water/oil emulsions. Asphaltenes can also adsorb onto different surfaces such as metals and minerals due to their favorable interactions with chemical species on or near the solid surface [4,5]. This adsorption can alter the wettability of clay and other mineral surfaces, affecting the production of oil from the reservoir rock matrix [1,6–10] and leading to the stabilization of water-in-oil emulsions [11–13]. Adsorption is affected by the non-uniformity of the mineral surfaces, competition by solvent, and multilayer attachment [5,14]. Several interactions determine the adsorption of asphaltenes on minerals, depending on the solvent medium, including electrostatic, van der Waals, acid–base, coordination, and hydrogen bonding interactions [4]. Near the onset of precipitation of asphaltenes, when coagulation of the colloidal particles begins, wetting alteration occurs by surface precipitation because of the aggregation of the colloidal asphaltenes on the mineral surface, which can precede flocculation of asphaltene in bulk [9,15].

The initial layer of asphaltenes adsorbed on mineral surfaces does not desorb easily, that is, most of the asphaltene in the initial layer are irreversibly attached to the mineral surface. They can only be removed to any extent if a much stronger solvent is used or if the surface chemistry is altered [4]. Despite this largely irreversible attachment, a recent review by Adams [4] found that conventional adsorption isotherms such as the Langmuir type or Freundlich type are the norm for modeling the dependence of the adsorption density versus the concentration of asphaltene in solution. The use of an adsorption isotherm implies a reversible process of interaction that reaches an equilibrium between surface species and solution species, and that there is little or no hysteresis between the adsorbate loading on the substrate surface and the adsorbate concentration in the solution during adsorption and desorption. If adsorption is not reversible then the adsorption isotherms are merely curve fittings with no fundamental validity or predictive value [16].

The irreversibility of adsorption of proteins, macromolecules, and other colloids has been studied extensively [17], but surprisingly the analogy between the adsorption of asphaltene to the adsorption of these better-characterized materials has not been discussed. In this context, irreversible adsorption is defined as a process in which the desorption of the adsorbed species occurs so slowly as to be undetectable during the time interval of the experiment. The implications of irreversible adsorption are illustrated in Fig. 1. In a typical experiment, mineral particles are mixed with an asphaltene solution, and allowed to equilibrate for a specified period of time. The amount adsorbed is then measured. Normally a series of such batch experiments at increasing initial asphaltene concentration is conducted to map out the adsorption-concentration curve. If desorption is attempted, by reducing the concentration of asphaltenes in solution, then little or no desorp-

tion occurs during the time interval of the experiment, and the adsorption density remains at the highest level obtained at the highest concentration. If the adsorption were partly reversible, then the desorption isotherm would show slightly lower adsorption density than the maximum but would still be well above the adsorption isotherm.

As illustrated in Fig. 1 the adsorption-concentration curve appears to follow a Langmuir isotherm, but the underlying process is not governed by equilibrium thermodynamics at all. For the case of proteins and macromolecules, the random-sequential adsorption (RSA) model provides a framework for interpretation of irreversible adsorption data [18]. The process is kinetically controlled, with initial random attachment of the polymer colloids to the surface. As the surface begins to fill, the available surface sites for adsorption decrease and the rate drops rapidly. The apparent Langmuir isotherm measured at a fixed time of contact (equilibration time) is the result of the fast adsorption regime followed by the asymptotic approach to surface saturation. The upper limit of surface coverage is determined by the “jamming limit”, where the repulsive forces between the polymer colloids exclude further adsorption. Depending on the shape of the polymer colloids on the surface, this limit may be 0.36–0.55 fractional surface coverage, even at very high polymer concentrations. For example, even the closest possible arrangement of disks on a planar surface will leave area uncovered.

Once attached to the surface, the macromolecules alter their structure, giving a flatter conformation with increased surface contact and much stronger adhesion [17]. Consequently, the rate of desorption is extremely slow, orders of magnitude slower than adsorption. Structural modification on the surface is less likely as the coverage of the surface approaches the maximum limit, because less surface is available for the polymer colloids to spread to increase surface contact. These characteristics can give partial reversibility of adsorption, and suggest that by first interrupting a non-equilibrium adsorption process, and then resuming the adsorption process at a later time, the results may not give a continuation of the same behavior.

Prior studies of adsorption of asphaltenes on clay minerals from good solvents, such as toluene, generally give results as illustrated by the representative adsorption data in Fig. 1, suggesting monolayer coverage [4,19–21]. Kaolinite is a layered aluminosilicate mineral, with one tetrahedral sheet linked through oxygen atoms to one sheet of alumina octahedra [22]. With these two types of external basal faces, broken bonds at particle edges, and cation exchange capacity resulting from isomorphous substitution near the surfaces, kaolinite can exhibit a strong affinity for organic compounds. It has been a popular choice for the study of asphaltene interactions because of its widespread occurrence, and its importance in oil sands.

Our hypothesis was that the adsorption of asphaltenes on kaolinite was governed by the kinetics of irreversible adsorption on the kaolinite surface with modification of the adsorbate structure on the surface, analogous to the adsorption of proteins. Adsorption density was determined at fixed contact times of 36 h for a range of kaolinite concentrations in asphaltene-toluene solutions. In order to better understand the interaction between asphaltene and kaolinite, two multiple contact methods were also used: multi-

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