Adsorption of asphaltenes from toluene on mineral surface

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Abstract

Undesirable adsorption of asphaltenes on rock minerals was studied. Asphaltenes are an important component of crude oil, being also natural surfactant stabilising water/crude oil emulsions. Owing to their chemical nature, asphaltenes are able to associate, form micelles and create a surface charge at the interface. Asphaltenes may be adsorbed on rock reservoir from the organic solvents in crude oil and as an organic colloid, they can adsorb electrolyte ions from aqueous solution. In order to simulate natural conditions we used asphaltenes from local drills, toluene as solvent and several typical oxides and carbonate rock components or minerals as adsorbents. Our study included natural Brazilian quartz, dolomite, calcite and kaolin, as well as pure oxides: Fe₂O₃ and TiO₂. The typical shape of asphaltene adsorption isotherms was obtained for all systems studied with the characteristic 'steps' which indicate changes in the state of asphaltene molecules in the solution and at the mineral surface. Those changes are related to the asphaltene association and further formation of hemimicelles and micelles. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is generally agreed that asphaltenes do not constitute a chemically identifiable class of compounds. They are defined basing on their method of precipitation i.e. as a fraction of bitumen that is soluble in light aromatic hydrocarbons but insoluble in low molecular weight paraffins such as pentane [1–4]. It is well known that asphaltenes consist of condensed aromatic rings, bound by alkyl chains and containing various functional groups i.e. carboxylic, hydroxyl, ether, ester, aldehyde, ketone, amine and amide. Nitrogen and oxygen atoms can also be present in aromatic structures analogous to pyridine, pyrazine, pyrrole, carbozole, indole or benzoic acid. Sulphur atoms are essentially present in thiophene and organic sulphur [5–7]. However, the composition of asphaltenes depends upon the origin of crude oil and the method of extraction [8–13]. Studies on asphaltene/mineral interactions yield new results in the field of environmental chemistry. During the enhanced oil recovery (EOR) procedures insoluble asphaltene particles may appear in the environment. They may also originate from uncontrolled split of oil products.
Owing to the presence of functional groups in the molecule, asphaltenes are able to create a surface charge at the interface. Since their interfacial activity, asphaltenes are of special interest from a colloidal point of view [2,10,14–35]. Asphaltenes as an organic colloid can adsorb electrolyte ions from aqueous solutions [1–3,36]. However, they may themselves be adsorbed from the organic phase on rock reservoirs [5,37–41]. These adsorption processes are further complicated by the behaviour of asphaltenes in organic solutions. The solvated asphaltene crystallites are the primary particles of the colloidal dispersed phase. These particles can associate and aggregate, forming various size particles depending on temperature, pressure and concentration [8,15,16,21,26–35,42,43]. In fact, asphaltenes are natural surfactants stabilising water/crude oil emulsion [21,22,44–52]. Thus, their adsorption on charged mineral surfaces could be considered as adsorption of ionic surfactants. It is well known that the shape of isotherms describing surfactant adsorption processes depends to a great extent on their critical hemimicelle concentration and critical micelle concentration (cmc) which mark the onsets of distinct isotherm regions [53–56].

One should notice that the subject of surfactant adsorption on polar surfaces from non-polar and weakly polar non-aqueous solutions is largely unexplored. Especially in the case of adsorption of such natural surfactants as asphaltenes, where mainly some experimental measurements were carried out, the nature of those processes is not well understood. Authors deal with aggregation, micellisation and multilayer formation, however, most papers conclude shortly that the isotherms are of Langmuir type and their conclusions are based only on the general shape of isotherms, without deeper insight into its course.

2. Materials and experimental methods

2.1. Materials

The asphaltenes used in this study were from Świdnik (near Lublin, Poland) crude oil. The oil had viscosity of 14.3³E (106 mm²s⁻¹, 96 cP) and a density of 881 kg m⁻³ at 293 K. The asphaltene content of the crude oil was about 2 wt.%. The asphaltenes were obtained from the crude oil as follows: the crude oil was mixed with five volumes of n-pentane and centrifuged at 2400 rpm for 10 min to precipitate the heaviest fraction. The precipitated fraction (hereafter called asphaltenes) was removed and the flocculant (n-pentane) was evaporated at 363 K in a rotary evaporation unit [2]. Elemental analyses of the asphaltene by Perkin–Elmer CHN 2400 showed the following: C 87.75, H 8.39, N 0.52%. The contents of Cl⁻ and HCO₃⁻ ions in the Świdnik reservoir brine were 45.03 g dm⁻³, 0.08 g dm⁻³, respectively.

For the further experiments, the asphaltenes were homogenised in the agate mortar.

Natural Brazilian quartz, dolomite and calcite, kaolin (Aldrich, Germany) as well as pure commercial oxides: iron oxide Fe₂O₃ (Apolda, Germany) and titania TiO₂ (Aldrich) being typical components of rock, were used as adsorbents. Before the experiments all adsorbents were washed to the supernatant value conductivity of redistilled water, i.e. about 1 μS cm⁻¹. Brazilian quartz was washed with 0.1 mol dm⁻³ HCl and water, kaolin with water, iron oxide and titania with 0.1 mol dm⁻³ NaOH and water. Precipitants were dried at 353 K for 24 h and crushed in the porcelain mortar.

The specific BET surface area of adsorbents determined by analysis of nitrogen adsorption was: for Brazilian quartz \( S_{BET} = 1.4 \) m² g⁻¹, for dolomite \( S_{BET} = 2.8 \) m² g⁻¹, for calcite \( S_{BET} = 1.12 \) m² g⁻¹, for kaolin \( S_{BET} = 16.4 \) m² g⁻¹, for iron oxide \( S_{BET} = 7.0 \) m² g⁻¹ and for titania \( S_{BET} = 9.2 \) m² g⁻¹.

The organic solvents, p.a. quality n-pentane and toluene, were supplied by Merck (Darmstadt, Germany).

2.2. Method

Static adsorption experiments were carried out at constant mass ratio of mineral to asphaltene solution (1:10) and concentrations (initial concentrations within the range 10–30000 ppm) were measured after 24 h equilibration at room temperature (293 K). The amount of adsorbed asphaltene-
nes was calculated from mass balance after determining the equilibrium concentration by UV/VIS absorption technique. The asphaltene solutions were diluted with toluene to the desired absorbance value.

3. Results and discussion

At first, we measured the spectra of asphaltene in toluene in the usual absorption linearity range, i.e. ABS < 1.5 and concentration below ~ 50 ppm. The curves are normalised with respect to the spectrum peak maximum. As we observed the gradual change of spectrum shape, we extended our measurements up to 333 ppm. For higher concentrations of asphaltene solution (over 200 ppm) an additional absorption peak (350–400 nm) appeared. The logical conclusion is that this peak is connected with some process dependent on the increasing asphaltene association in solution. This concentration is well below the CMC of asphaltenes (~ 3000 ppm [15,16,29]) where the association process is more or less complete, whereas the above phenomenon may manifest just the onset of an association process. (We could not follow our experiments to higher concentration range because of our spectrophotometer set-up and very high absorption coefficient value).

In order to optimise our adsorption measurements, we also determined the spectrum wavelength, where the best correlation of calibration line may be obtained (Fig. 1). We plotted ABS versus concentration in log–log co-ordinates for spectrum wavelengths λ: 240, 270, 290, 300, 350 and 400 nm, as well as for the absorption peak maximum (~ 288 nm, denoted as max) and the difference between absorption at peak maximum and λ = 400 nm (max-400). We found that the widest range of log–log linearity is obtained for the peak maximum. We used this wavelength and calibration in all subsequent adsorption experiments.

The adsorption experiments were carried out for a wide range of initial concentrations and six solids. The following figures present the obtained isotherms in two kinds of co-ordinates-adsorption (a) versus equilibrium concentration (c) allows for easy analysis of isotherm course in the medium and high concentration range. However, the log–

![Fig. 1. Absorbance (ABS) vs. concentration (c) calibration lines in log–log co-ordinates for various spectrum wavelengths (240, 270, 290, 300, 350 and 400 nm), absorption maximum (max) and the difference between peak maximum and absorption at 400 nm (max-400). Solid lines, large points and boldface descriptions correspond to plots with highest linearity (λ_max-thick line; 290, 300, 350 and 400 nm).](image-url)
where \( a \) is adsorption value, \( a_m \) is monolayer capacity, \( c \) is concentration, \( K \) is adsorption equilibrium constant, \( K_n \) is Kiselev association constant and \( m \) is heterogeneity coefficient.

The results of fitting (solid lines in Fig. 2) show that such explanation is quite reasonable. However, one cannot take the optimisation parameters \( (a_m = 38 \text{ mg g}^{-1}, K = 2.1 \times 10^4 \text{ ppm}^{-1}, m = 0.75, K_n = 3.1) \) as physicochemical ones, because the GF–K model does not take into consideration the multilayer formation and is an oversimplification of the true micellisation process.

In order to further explain the influences of various parameters of isotherm on its form, we presented the experimental adsorption data in one of the linear Langmuir co-ordinates, \( a \) versus \( a/c \) (Fig. 3, white circles). In this form, the whole Langmuir isotherm region is compacted to the line segment (optimised dotted line) determined by maximum adsorption \( (a = a_m, c \to \infty, a/c = 0) \) and zero adsorption \( (a = 0, c = 0, a/c = a_m K) \) [59,60]. Thus, all discrepancies from the Langmuir model (i.e. ideal behaviour both in the surface and bulk phases) are clearly visible. The optimised GF–K is represented by a solid line—clearly the fitting quality is much better than in the case of Langmuir isotherm. The dashed line corresponds

\[
a = a_m \left( \frac{K c[1 + K_n (a/a_m)]}{1 + K c[1 + K_n (a/a_m)]} \right)^m
\]  

(1)

Fig. 2. Adsorption isotherm of asphaltenes on Brazilian quartz (white circles) compared with optimised GF–K isotherm (solid line and Eq. (1), see text) in \( a \) vs. \( c \) and log–log co-ordinates. Dashed line corresponds to the Freundlich isotherm fitted to the experimental points in low-concentration range.

log plot exposes lower concentrations and general adsorption trends over wide concentration range. We also fitted Freundlich (F) isotherm to the low concentration ranges of all isotherms.

The adsorption of asphaltenes on Brazilian quartz is presented in Fig. 2. In the standard, adsorption–concentration plot, we can see seemingly Langmuirian shape of isotherm with small steps. However, in log–log co-ordinates we can observe that for the low concentration range adsorption is far from Langmuir or Henry behaviour: isotherm slope should be equal to 1, however, it is close to 0.75 (typical Freundlich) [57,58]. Moreover, we can see small upward isotherm inflection (log \( c \sim 2–2.5 \)), which suggests the existence of some kind of lateral interaction. Taking into account the shape of isotherm together with the knowledge about the nature of micellisation process we tried to fit the Generalised Freundlich (GF) isotherm (Freundlich-type heterogeneity in monolayer adsorption) combined with the simplified Kiselev association model [57]:

Fig. 3. Isotherm of adsorption of asphaltenes on Brazilian quartz (white points) presented in the linear Langmuir co-ordinates: adsorption (\( a \)) vs. adsorption/concentration (\( a/c \)). Solid line denotes fitted GF–K line and dotted line refers to the Langmuir isotherm. The GF–K component isotherms, Kiselev (dashed line) and GF model (dashed-dotted line) are calculated according to the GF–K optimised parameters (see text).
The next figure (Fig. 5) presents the isotherm in the $a$ versus $a/c$ co-ordinates. For high and medium adsorption one can observe a series of short linear sections which correspond to isotherms steps. However, the presence of heterogeneity is far less pronounced in contrast to the obvious ‘bulge’ at adsorption $< 50$ mg g$^{-1}$ clearly related to the lateral interactions. The course of isotherm of adsorption on titania differs from that on quartz, however, as the surface topography can play a key role in lateral interactions [57], we do not try to explain those differences on the basis of the presented isotherms alone.

The adsorption of asphaltenes on $\text{Fe}_2\text{O}_3$ is presented in Fig. 6. We can see another typical asphaltene adsorption isotherm ($a$ vs. $c$ plot) with steps (a small, sharp one at $\sim 300$ ppm and another one above 4000 ppm). In the log–log co-ordinates the isotherm course is largely similar to the adsorption on titania.

In the following figures, we present the adsorption of asphaltenes on carbonates: on calcite (Fig. 7) and on dolomite (Fig. 8). Again, we can observe those typical adsorption steps, however, the slopes of low-concentration isotherms in log–log co-ordinates are 0.83 and 0.97, respectively. These values are lower that 1 (Langmuir or Henry isotherms at $c \to 0$), though much higher than 0.75 found for quartz. It suggests some surface heterogeneity effects, however, one cannot compare heterogeneity to the Kiselev model (GF–K without heterogeneity, $m = 1$) and the dotted-dashed one is calculated according to the GF model (GF–K without association, $K_n = 0$). Both lines were calculated with the same parameters as the fitted GF–K line. It is easy to state that the heterogeneity of the GF–type influences the isotherm mainly for the low adsorption region (high $a/c$ values) and that the association phenomena are important mainly at medium and high adsorption (medium and low $a/c$ values). It should be noted that in the case of large steps at high adsorption the $a$ versus $a/c$ lines will also display a series of short linear steps.

The adsorption of asphaltenes on titania is presented in Figs. 4 and 5. In Fig. 4 ($a$ vs. $c$ plot) we can see a typical isotherm with steps (a small, sharp one at $\sim 600$ ppm and another one $\sim 3000$ ppm, i.e. 0.3%). In the log–log co-ordinates (Fig. 4), we can observe that for the low concentration range adsorption is far from Langmuir or Henry behaviour. The isotherm slope should be less or equal to 1, however, it is much larger (close to 1.4), which is typical of the inflection range of adsorption with strong lateral interactions [57]. For concentrations above 100 ppm (log $c \sim 2$) we can see a series of ‘irregularities’ that correspond to the above described steps, which refer to the various stages of association/micellisation process.
Fig. 6. Adsorption isotherm of asphaltenes on Fe$_2$O$_3$ (white circles and solid lines) in $a$ vs. $c$ and log–log co-ordinates. Dashed line corresponds to the Freundlich isotherm fitted to the experimental points in low-concentration range.

Fig. 7. Adsorption isotherm of asphaltenes on calcite (white circles and solid lines) in $a$ vs. $c$ and log–log co-ordinates. Dashed line corresponds to the Freundlich isotherm fitted to the experimental points in low-concentration range.

Fig. 8. Adsorption isotherm of asphaltenes on dolomite (white circles and solid lines) in $a$ vs. $c$ and log–log co-ordinates. Dashed line corresponds to the Freundlich isotherm fitted to the experimental points in low-concentration range.

Fig. 9. Adsorption isotherm of asphaltenes on kaolin (white circles and solid lines) in $a$ vs. $c$ and log–log co-ordinates. Dashed line corresponds to the Freundlich isotherm fitted to the experimental points in low-concentration range.

ergogeneities on this basis alone, as this effect is ‘masked’ by lateral interactions (association etc.), when the latter effect depends also on the surface topography and structure [57,59,60].

In Fig. 9, the adsorption of asphaltenes on kaolin is presented. Two gentle steps can be seen

(at $\sim 600$ ppm and at $\sim 3000$ ppm) in $a$ vs. $c$ plot. The slope of log–log isotherm is close to unity (i.e. 0.97) in the low concentration range.

For the adsorption systems studied, we can also observe the high slope coefficient (in log–log co-ordinates) in the higher adsorption region which is characteristic of multilayer formation [57,58].
and hemimicelle formation [54,55,61]. The only exception is adsorption on quartz (Figs. 2 and 3), where the isotherm practically levels-off, and to some extent on Fe₂O₃ (Fig. 6), where the second range of high slope begins at relatively high concentrations.

The typical shape of asphaltene adsorption isotherms was obtained for all the systems studied, with characteristic 'steps' which indicate changes in the state of asphaltene molecules in the solution and at the mineral surface. Those changes are related to the asphaltene association and further formation of hemimicelles on the mineral surface. As a result of these phenomena the character of rock mineral surfaces may change from hydrophilic to hydrophobic.

4. Conclusions

Our adsorption measurements show that although very often adsorption of asphaltenes on minerals is described as 'Langmuir type' it is in fact quite distant from that simple model. All such adsorption isotherms contain initial lines of Freundlich characters with slope coefficients or/ and inflections characteristic of lateral interactions, as well as multiple steps that may be related to surface phase reorientation, multilayer formation, or hemimicelle formation.

References