Adsorption of asphaltenes from toluene on quartz and silica-rich soils

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Adsorption of asphaltenes from tolune on quartz and silica-rich soil fractions is investigated. Such process mimics the phenomena occurring during oil spills and in natural oil reservoirs.

In order to simulate natural conditions we used pentane-precipitated asphaltenes obtained from local crude oil (drills at Świdnik, near Lublin), toluene as solvent and natural Brazilian quartz as model adsorbent. The results obtained for model system are compared with asphaltene adsorption on silica-rich soil fractions from the Lublin region.

The isotherm features are typical for asphaltene adsorption. Characteristic "steps" – often masked by heterogeneity of adsorbent and complex composition of natural asphaltenes – indicate changes in the state of asphaltene molecules in the solution and at the mineral surface and may be related to the asphaltene association and formation of hemimicelles and micelles.

1. INTRODUCTION

Asphaltenes are important component of crude oil, being also natural surfactant stabilising water/crude oil emulsions [1]. Owing to their chemical nature, asphaltenes are able to associate, form micelles and create surface charge at the interface [2]. Asphaltenes, as an organic colloid, can adsorb electrolyte ions from aqueous solution. Moreover, they may be adsorbed on rock reservoir from the organic solvents in crude oil [3].

One should expect that these adsorption processes be further complicated by the behaviour of asphaltene in organic solutions. The solvated asphaltene crystallites are the primary particles of colloidal dispersed phase. These particles can associate and aggregate forming large particles dependent on

temperature, pressure and concentration (it is well known that asphaltenes form micelles in aromatic organic solvents at concentration higher than CMC) [4-6].

2. EXPERIMENTAL

In order to simulate natural conditions we used pentane-precipitated asphaltenes [1] obtained from local crude oil (drill at Świdnik, near Lublin), toluene as solvent and natural Brazilian quartz as model adsorbent (the specific BET surface area of quartz determined by analysis of nitrogen adsorption was SBET =1.4 m2g-1) The results obtained for model system are compared with asphaltene adsorption on silica-rich soil fractions from Lublin region (with SBET from 1.9 to 50 m2g-1).

The colloidal and electrochemical properties of our asphaltenes in aqueous solutions are described elsewhere [1]. Our study included typical silica-rich soils from the Lublin region like black earth, brown soil, and pararendzina soil. Main physicochemical properties of these soils were determined by S. Chibowski, J. Zygmunt and Z. Klimowicz [7-9]. The basic adsorption properties (nitrogen adsorption, adsorption of surfactants from water solution, acidity, etc.) of several soil fraction were studied by B. Kowalczuk [10] and A.W. Marczewski [11].

We decided to use only certain fractions with highest adsorption capacity, as other fractions should have limited impact on total adsorption (Table 1; codes are the same as in [3,12]).

The static adsorption experiments were carried out at constant mass ratio of mineral/soil to asphaltene solution (1:10) and concentrations (initial concentrations within the range 10 - 40000 ppm) were measured after 24 hr. equilibration at room temperature (293K). The amount of adsorbed asphaltene was calculated from mass balance after determining the equilibrium concentration by UV/VIS absorption technique.

3. RESULTS AND DISCUSSION

The adsorption experiments were carried out for a wide range of initial concentrations and four adsorbents: Brazilian quartz and three silica-rich soil fractions.

The Figures 1, 3, 5 and 7 present the obtained isotherms in two kinds of co-ordinates. The plot of adsorption (a) vs. equilibrium concentration (c) allows for easy analysis of isotherm course in the medium and high concentration range. However, the log-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 (broken lines).

Another set of figures (Figures 2, 4, 6 and 8) presents data in the linear Langmuir co-ordinates, a vs a/c.

The adsorption of asphaltenes on Brazilian quartz is presented in Figures 1 and 2. In the lower part of Figure 1 (a vs. c) we can see seemingly Langmuirian shape of isotherm with small steps, however in log-log co-ordinates (upper part) we can observe that for the low concentration range adsorption is far from Langmuir or Henry behaviour: isotherm slope should tend to 1, however it is close to 0.75 (typical Freundlich). Moreover, we can see small upward isotherm inflection (log c ~ 2 - 2.5), which suggests the existence of some kind of lateral interaction.
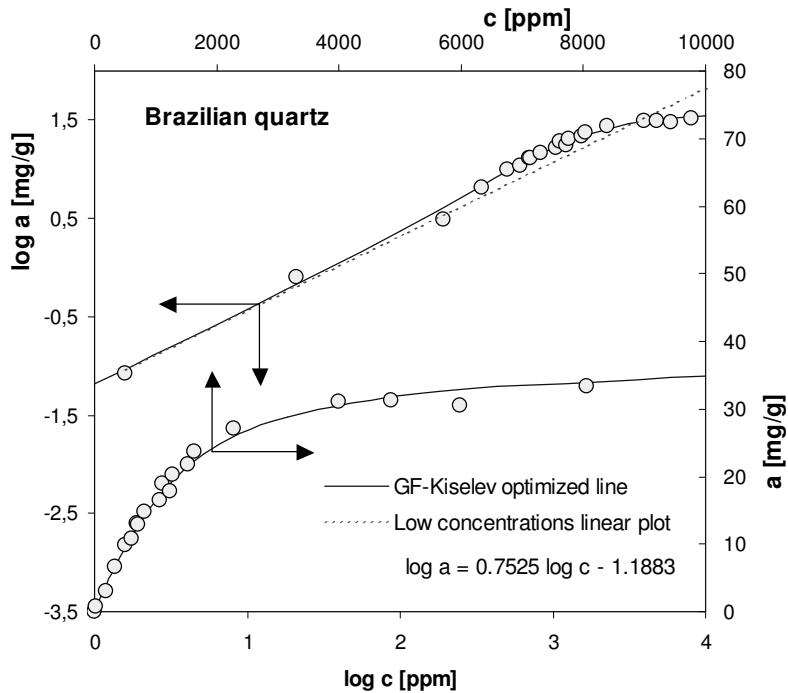

Fig. 1. Adsorption of asphaltenes on Brazilian quartz.

Tab. 1. Granulometric composition and some physicochemical properties of the silica and silica-rich soil fractions.

| Adsorbent (Mineral or Soil)	Code	Bulk density [g/cm^3]	Particle size [mm]	Mass fraction X_w	S_{BET} [m^2/g]	Fractional BET surface area	Pore volume, V_p [cm^3/g]	Micropore volume [cm^3/g]	Mean pore size [Å]
Brazilian quartz	Q				1.4		0.0013	0	176
Black earth soil	G1	1.026		1					
silica-rich fraction	G1f3		0.02-0.01	0.138	1.9	0.244	0.0042	0	89
Brown soil	G4	1.2426		1					
silica-rich fraction	G4f2		0.02-0.01	0.183	7.422	0.2141	0.0139	0	75
Pararendzina soil	G6	1.1694		1					
silica-rich fraction	G6f4		<0.01-0.005	0.113	50.08	0.084	0.118	0.0019	94
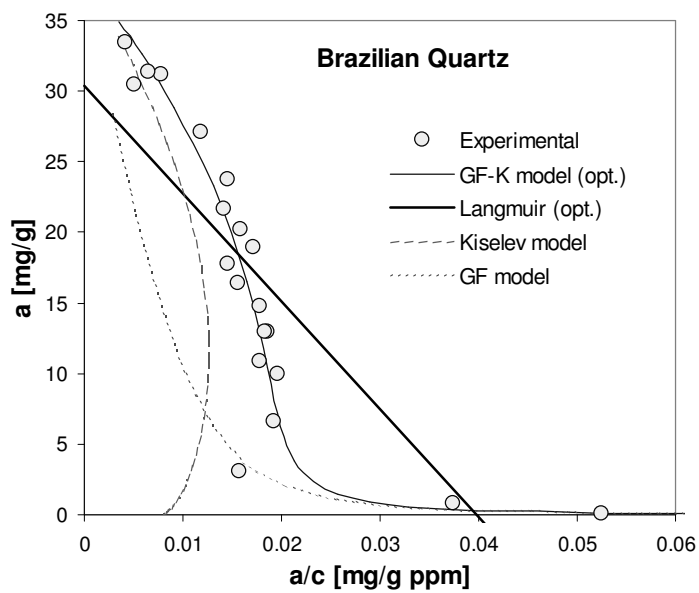
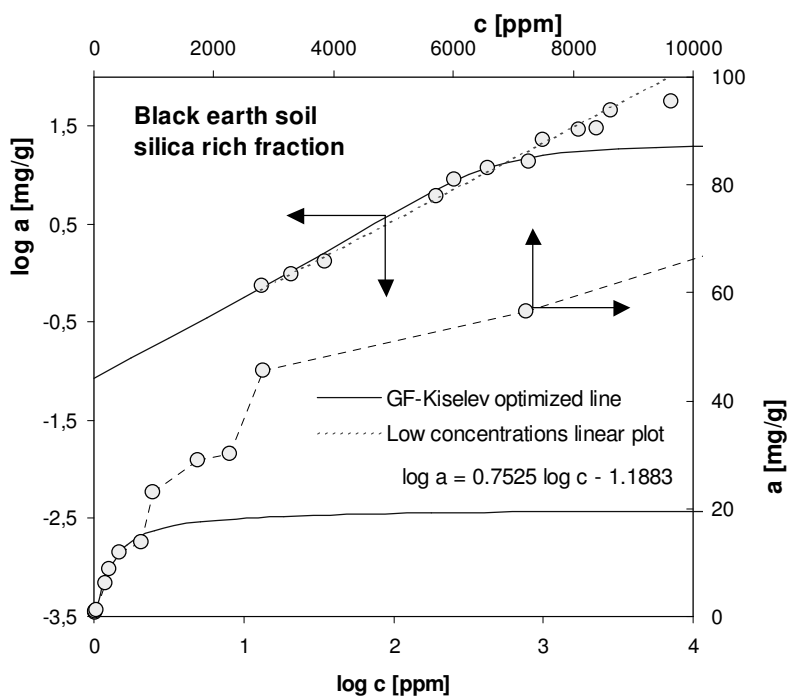Fig. 2. Adsorption of asphaltenes on Brazilian quartz – linear Langmuir plot.

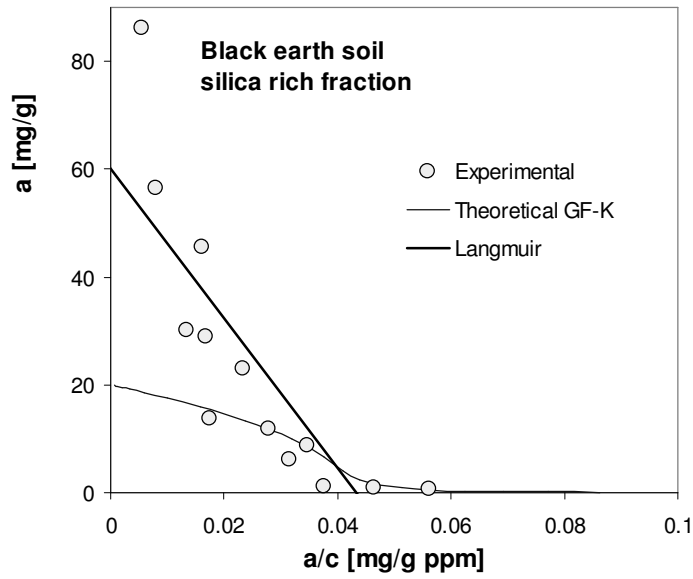Fig. 3. Adsorption of asphaltenes on black earth soil fraction.

Fig. 4. Adsorption of asphaltenes on black earth soil – linear Langmuir plot.
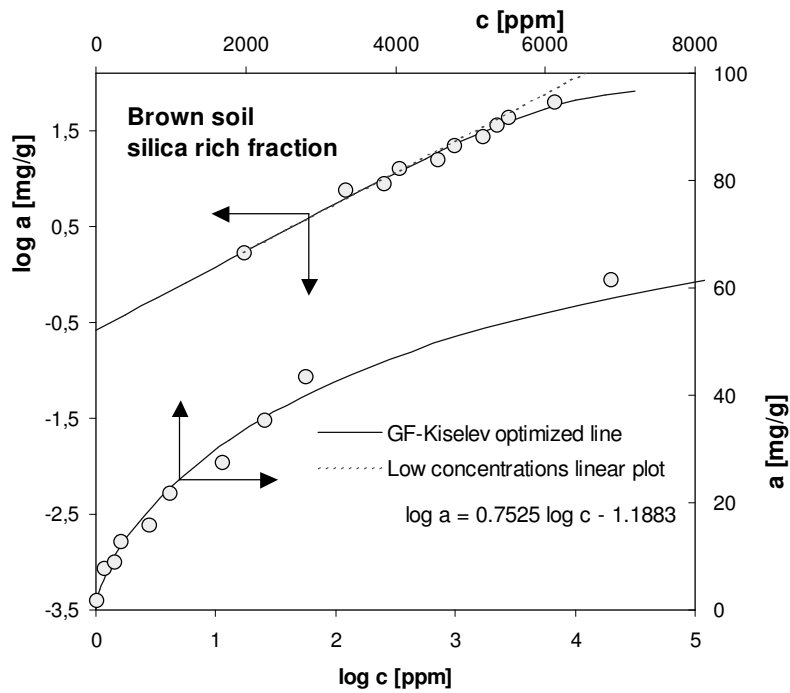

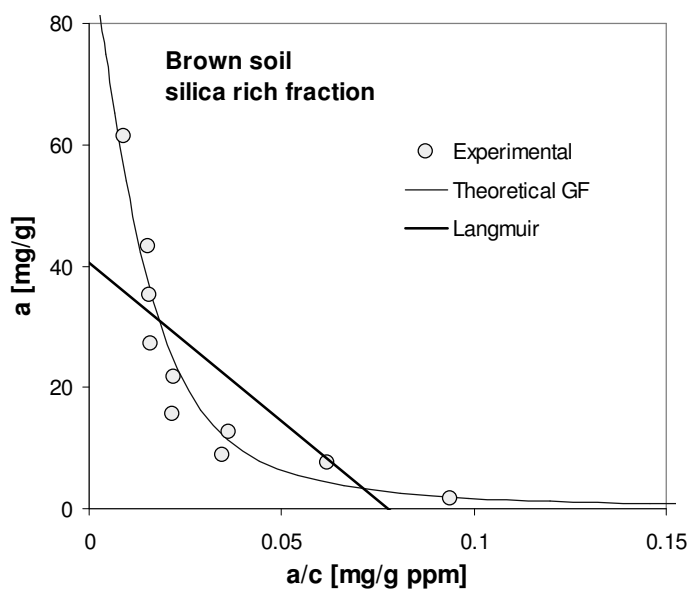Fig. 5. Adsorption of asphaltenes on brown soil fraction.

Fig. 6. Adsorption of asphaltenes on brown soil – linear Langmuir plot.
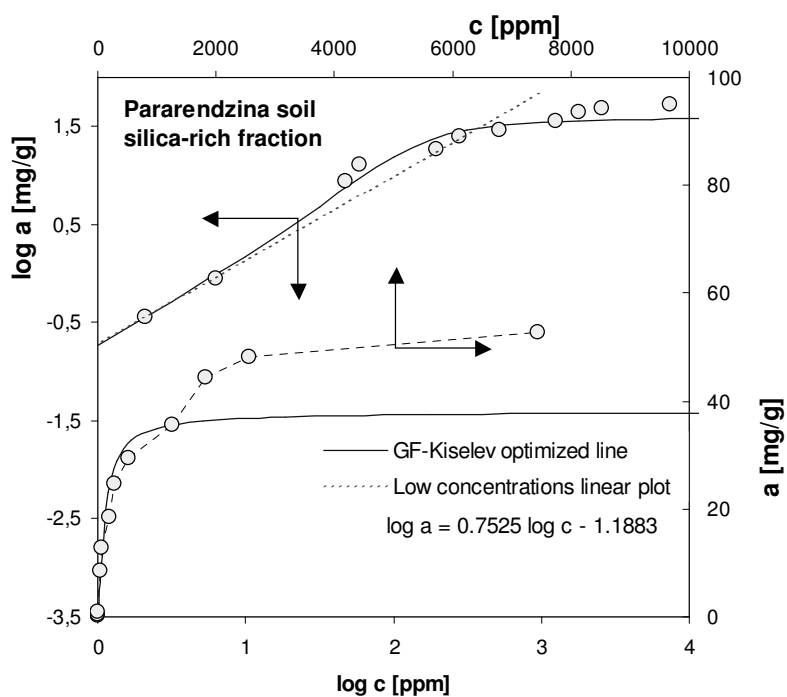

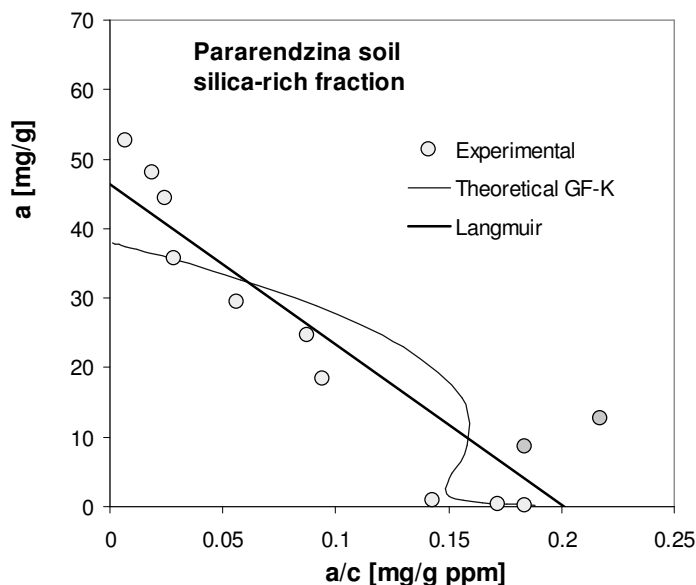Fig. 7. Adsorption of asphaltenes on pararendzina soil fraction.

Fig. 8. Adsorption of asphaltenes on pararendzina – linear Langmuir plot.

Taking into account the shape of isotherm together with the general 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:

Generalised Freundlich – Kiselev eq.:

$$a = a_m \left(\frac{Kc \cdot f_{int}(\theta)}{1 + Kc \cdot f_{int}(\theta)} \right)^m \quad \text{where} \quad f_{int} = 1 + K_n \theta \quad \text{and} \quad \theta = a/a_m$$

where a is adsorption value, am is monolayer capacity, c is concentration, K is adsorption equilibrium constant, Kn is Kiselev association constant and m is heterogeneity coefficient.

The results of fitting (thin solid lines in Figures 1 and 2) show, that such explanation is quite reasonable. However, one cannot treat the optimisation parameters (am=38 mg/g, K=2.1·10-4 ppm-1, m=0.75, Kn=3.1) as physicochemical ones, because the GF-K model does not take into consideration the multilayer formation and is a serious oversimplification of the true micellisation process.

In order improve our understanding of 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 vs a/c (Figure 2, circles). In this form, the whole Langmuir isotherm region is compacted to the line segment (optimised Langmuir: thick solid line) determined by maximum adsorption (a=am , c→∞, a/c=0) and zero adsorption (a=0, c=0, a/c=amK). 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 thin solid line - clearly the fitting quality is much better than in the case of Langmuir isotherm. The dashed line corresponds to the Kiselev model (GF-K without heterogeneity, or m=1) and the dotted line is calculated according to the GF model (GF-K without association, or Kn =0). Both lines were calculated with the same parameters as the fitted GF-K line and are not fitted to the experimental data separately. It is quite clear that the heterogeneity of the GF-type influences the isotherm mainly at low adsorptions (low a and high a/c values) and that the association phenomena are important mainly at medium and high adsorptions (medium and low a/c values).

Some important adsorbent parameters as well as the results of fitting are presented in the Table 2. In subsequent pairs of figures the fitted isotherms and experimental data of asphaltene adsorption on siliceous soil fractions are presented: Figures 3 and 4 on fraction of black earth soil, Figures 5 and 6 on fraction of brown soil and finally Figures 7 and 8 on fraction of pararendzina soil.

The typical shape of asphaltene adsorption isotherms was obtained for all systems studied, with characteristic „steps" which indicate changes in the state of asphaltene molecules in the solution and at the soil surface. Those changes are related to the asphaltene association and further formation of hemimicelles on the mineral surface. As the effect of these phenomena the character of soil surfaces may change from hydrophilic to hydrophobic [3, 13-17].

Generally, a weak correlation of adsorption monolayer capacity am with specific surface area SBET and mesopore volume Vmeso is observed. This problem is especially pronounced if we compare data for Brazilian quartz with parameters obtained for G6f4 soil fraction with especially high surface area and mesopore volume. However, it must be said, that the source of this discrepancy is mainly the large size of typical asphaltene molecule (or at larger concentrations – particle) that cannot fit into smaller pores (often larger surface area).

Tab. 2. Best-fit parameters of GF-K isotherm (equ. X) for adsorption of asphaltenes on quartz and silica-rich soil fractions (see Table 1).

Code (see Tab. 1)	S_{BET} [m^2/g]	V_{meso} [cm^3/g]	a_m [mg/g]	m	K [ppm^{-1}]	K_n	best-fit range[ppm]
Q	1.4		38	0.75	$2.1 \cdot 10^{-4}$	3.1	< 10000
G1f3	1.9	0.0042	20	0.80	$1.1 \cdot 10^{-3}$	2.2	< 1000
G4f2	7.4	0.0139	95	0.66	$1.32 \cdot 10^{-4}$	0*	< 7000
G6f4	50	0.118	38	0.86	$2.1 \cdot 10^{-3}$	4*	< 3000
average				0.77	$5 \cdot 10^{-3}$	~2	

* Unusually high value of K_n (G6f4) may be attributed to high susceptibility of fitting procedure to data scatter, however $K_n=0$ (G4f2) may result from masking of lateral interactions by higher heteroheneity (m=0.66) than in other cases.

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