Adsorption Behavior of Asphaltenes and Resins on Kaolinite

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ABSTRACT: Recent studies have shown that *n*-C7-precipitated asphaltenes adsorb onto nanoparticles to produce isotherms that are significantly influenced by the dispersed states of both the adsorbate and adsorbent. In the present work, we investigate this behavior further by determining the adsorption of asphaltene and resin fractions isolated from four different sources onto kaolinite using the depletion method in toluene. Treated conventionally (amount adsorbed, Γ , versus equilibrium bulk concentration, c_e), adsorption isotherms for fixed initial concentrations (c_o) of C5 and C7 asphaltenes and variable kaolinite mass (m_s) are found to be Type I as classified by IUPAC, whereas under the same experimental conditions C5-C7 resins exhibit Type III behavior. By fixing m_s and varying c_o , however, Type II isotherms are produced by the resins. All the adsorption results for the same fraction type were found to be very similar, irrespective of the source. The Types I and III isotherms are described very well by the thermodynamic solid-liquid equilibrium (SLE) model of Montoya et al. (*Energy Fuels* **2014**, *28*, 4963–4975) based on association theory of Talu and Meunier (*AIChE J.* **1996**, *42*, 809–819). Individual isotherms (Γ versus c_e) are well-fitted by a shifted Langmuir equation for asphaltenes, and by a general Freundlich (power law) relationship for resins. The SLE results verify that in toluene solution the adsorption behavior is complicated by concentration-dependent nanoaggregation of asphaltene species, whereas resin-resin interactions are weaker, but accompanied by adsorbent particle aggregation. On the other hand, when the adsorption data for each fraction type is re-plotted in terms of the ratio of the experimental parameter c_o/m_s , as originally done by Wang et al. (*Colloids Surfaces A: Physicochem. Eng. Aspects* **2016**, *504*, 280–286), each set of data merges to a single isotherm which is reasonably well approximated by a Langmuir-type relationship (we term this a “pseudo-Langmuir equation”), which allows the maximum adsorption to be determined for the different adsorbate/adsorbent systems. The average maximum adsorbed amounts calculated in this way for each of the component types are very similar, being slightly larger for C7A compared with C5A, with the values for the C5-C7R fractions being generally lower and more variable, possibly reflecting some source dependence.

1. INTRODUCTION

Elucidation of the molecular structure of asphaltenes has reached a significant point in its journey following the report by Schuler et al. of the first atomic resolution images of petroleum and coal asphaltenes using a combination of atomic force and scanning tunneling microscopies.¹ The images offer a profound insight into the molecular architecture of the asphaltenes, and confirm their polycyclic aromatic nature proposed many decades ago.

However, whilst their structure is now conclusively unfolding, asphaltenes pose further questions which are especially relevant to their behavior in operational set-

tings. Being the least soluble components within the crude oil, polycyclic aromatic asphaltenes are inherently unstable in a predominantly saturated hydrocarbon environment and therefore rely on favorable interactions with other oil components to remain well-dispersed. Their most natural allies in this respect have historically been considered to be the aromatics and resins fractions.^{2,3}

Dickie and Yen considered that resins “inhibit” the aggregation process of polar asphaltenes in the non-polar oil.⁴ Resins are soluble in toluene and some *n*-alkanes, and their phase separation boundary with asphaltenes is determined by the alkane chain length.^{5,7} For example,

C5-C7 resin fractions, which we consider later, are soluble in *n*-heptane (*n*-C7) but insoluble in *n*-pentane (*n*-C5), asphaltenes being insoluble in both.

It has long been thought that resins act as peptizing agents for asphaltenes by increasing their colloidal stability through inhibiting asphaltene self-association and successive aggregation.⁸⁻¹³ Thus, destabilization of asphaltenes by the addition of paraffinic solvents, which results in aggregation and precipitation, is often explained by the selective dissolution or desorption of the stabilizing resins from the asphaltene surfaces.¹²

Compositionally, much also remains to be discovered as far as the resin components are concerned. As with asphaltenes, it is considered that the composition and properties of resins depend on their source. This has been reflected in their dielectric properties and interactions with asphaltenes.^{6,14} It has previously been reported that each resin molecule contains an average of 12 aromatic carbon atoms, corresponding to two/three aromatic rings, with the remainder of the carbons being present as aliphatic (naphthene) rings (~6) and chains.¹⁵ However, a more widely-held view is that, compared to asphaltenes, resin molecules are smaller in size and molecular weight, and contain an average of between one and six aromatic rings. Resins also possess significantly lower heteroatom content than asphaltenes, with a lower propensity for self-association.^{5,8,9} Using SARA (saturates, aromatics, resins and asphaltenes) fractionation combined with Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), Cho et al. identified a greater abundance of nitrogen-containing saturated and aromatic species present in the resins fraction than are found in the corresponding, predominantly aromatic asphaltenes.¹⁶

Adsorption of the heavier polar components from crude oil governs many aspects of recovery and production operations. Generally, the effects produced are undesirable, since they can lead to such consequences as deposition,¹⁷ both upstream¹⁸ and downstream,¹⁹ wettability modification,^{20,21} and emulsion stabilization,²²⁻²⁴ and for these reasons considerable effort has been directed at understanding the behavior of crude oils and their constituents at interfaces.

The adsorption of asphaltenes at different interfaces has received considerable attention, and has been thoroughly reviewed recently by Adams.⁸ In general, the results from adsorption studies carried out over the years have been found to be consistent with classical adsorption models, as we have also demonstrated recently for quartz sand.²⁵ However, notwithstanding the general principles set out in previous studies, crude oil components are not 'classical' surface-active species as was pointed out by Czarnecki et al. in connection with their role in water-in-oil emulsion stabilization,^{22,23} and it might therefore be expected that adsorption could also depart from the expected models on other surfaces. Herein, we report results from batch adsorption experiments on asphaltenes and resins that follow significantly different trends, and, as will be seen, lend support to recent work reported by Guzmán et al.³ and Wang et al.²⁶ Fur-

ther, they relate to the fundamental understanding of asphaltene solution and surface behavior, as well as to applied areas.

In the aforementioned studies,^{3,26} both groups used *n*-C7 asphaltenes for the adsorption experiments. Guzmán et al.³ isolated their asphaltenes from two unspecified extra heavy oils and studied adsorption from toluene or heptol (60/40 v/v *n*-heptane/toluene) on silica nanoparticles (~154 nm diameter), fumed silica (~7 nm diameter) and nano-sized magnetite (~97 nm diameter). Wang et al.²⁶ isolated their *n*-C7 asphaltene sample from an Athabasca steam-assisted gravity drainage (SAGD) recovery operation and determined adsorption from toluene on kaolinite.¹¹ Each group independently identified that adsorption was dependent on the initial starting concentrations of adsorbent and adsorbate, and not the equilibrium adsorbate concentration, as required by classic reversible adsorption models, typified by the Langmuir model.¹² Notably, Guzmán et al. conducted batch adsorption experiments in two different ways, namely, fixed adsorbent concentration + variable initial adsorbate concentration (method 1), and fixed initial adsorbate concentration + variable adsorbent concentration (method 2).³ The adsorption data were then analyzed using the molecular association adsorption model of Talu and Meunier,²⁸ which they had previously adapted and termed the solid-liquid equilibrium (SLE) model.²⁹ The SLE model satisfactorily described IUPAC Type I isotherms (from method 1) and Type III isotherms (from method 2).

On the other hand, the approach taken by Wang et al. was entirely empirical, but found substantially similar behavior, leading to the conclusion that adsorption of *n*-heptane-precipitated asphaltenes onto kaolinite from toluene solution did not depend on the equilibrium solution concentration as required for thermodynamic adsorption models.²⁶ Significantly, however, this study also showed that the adsorption data reduces to a single isotherm when the adsorbed mass is plotted against the initial asphaltene/kaolinite mass ratio. The authors therefore concluded that for their kaolinite/*n*-C7 asphaltene system, adsorption was irreversible and kinetically-controlled.²⁶

Whilst the adsorption of asphaltenes at solid³⁰ and aqueous³¹ interfaces has been considered to be irreversible process for many years,⁸ this new work has increased the significance for solid surfaces, since it implies very low, or non-existent, desorption rates.^{26,30}

The original focus of the present experimental study was the comparative investigation of the adsorption behavior of *n*-C5-precipitated asphaltenes (C5A) and their *n*-C7-precipitated asphaltene (C7A) counterparts. In this way, effects of the C5-C7R resin fraction differentiating them (eq. 1) may become apparent, as, for example, Dufour et al. found with respect to asphaltene stabilization against *n*-heptane precipitation.³²

In the present work, therefore, we have considered the adsorption from toluene solution of C₅A, C₇A and C₅-C₇R fractions isolated from four different sources onto kaolinite. We envisaged that further information on the role of asphaltene-resin interactions may also be obtained from a practical standpoint, if not from a fundamental level. It was apparent to us that even allowing for the extensive asphaltene literature available, adequate physical models which consider interactions between asphaltenes and resins are still tentative at best, whilst being ignored at worst, and adsorption studies may help to provide further insight. Kaolinite was selected as the adsorbent for this study because of its use in previous adsorption studies,^{3,8,26} as well as its relevance to oil sands recovery and processing, where along with other clay minerals, it is a constituent of tailings ponds as well as being susceptible to wettability alteration by asphaltenes.^{20,21,27} Toluene was used as the adsorption medium to ensure good solvency conditions for all the fractions, and to maintain some commonality with the related studies. The use of mixed aromatic/aliphatic solvents, such as heptol, being more representative of crude oil maltenes, would be the subject of future investigations.

2. EXPERIMENTAL SECTION

2.1. Materials. The four different sources from which the asphaltene and resin fractions were isolated are given in Table 1. One source was received in its natural state as a preserved oil sands core; one was a sample of bitumen produced from a different reservoir in a pilot steam-assisted gravity drainage (SAGD) project; one was a sample of bitumen that had been ‘topped’ at 550 °C to remove lighter components; and one was a refinery asphalt residue produced by the Residuum Oil Supercritical Extraction (ROSE™) process. The last of these would have been produced from a blend of crude oils, whereas the bitumen samples will be representative of the production from specific reservoirs.

Table 1. Details of the primary sources of asphaltenes and resins used in this study

Sample	Description/ received as	Source
As ₁	Pellets of highly asphaltenic refinery residue	ROSE™ (Residuum Oil Supercritical Extraction) pentane deasphalting process, Meraux Refinery, LA, USA
B ₁	Natural bitumen, received as frozen oil sands core	Athabasca, Canada
B ₂	Natural bitumen previously recovered by steam-assisted gravity drainage	Athabasca, Canada

R ₁	Bitumen residue ‘topped’ at 550 °C to remove lighter components	Cold Lake, Alberta, Canada
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n-Heptane (Chromosolv for HPLC ≥ 98 %) was from Sigma-Aldrich Ltd, and *n*-pentane (98%, Reagent Grade) and toluene (Analytical Reagent grade, low in sulfur) were from Fisher Scientific, UK, and were used as-received. The adsorbent, natural kaolinite, was obtained from Sigma-Aldrich (batch number BCBN9036V). Kaolinite from the same source has been reported to comprise particles in the range 0.1–4 µm with a BET specific surface area (A_s) of 17.2 m²/g.³³ The BET value for the present sample is 7.37 ± 0.05 m²/g (determined by the Oxford Materials Characterisation Service, Oxford, UK). In fact, A_s values for natural kaolinites quoted in the literature based on BET determinations,^{33–35} inverse gas chromatography,³⁶ or estimated from particle size³⁷ vary considerably, in part due to the state of aggregation.³⁸

2.2. Isolation of oil fractions. Fig. 1 shows the scheme used to prepare the various oil fractions. *n*-Pentane and *n*-heptane were used to derive C₅A and C₇A, respectively, as well as the corresponding maltenes (C₅M and C₇M). A combination of these two solvents was used to isolate the intermediate resin fraction C₅-C₇R by washing the precipitated C₅A with *n*-C₇. These resins will therefore fall into the type I classification of Navarro et al.³⁹

Figure 1. Separation schemes for obtaining C₅A, C₅M, C₇M, C₇A(1 and 2) and C₅-C₇R fractions.

2.2.1. Soxhlet extraction of bitumen from oil sand. In the case of the oil sand, bitumen was first recovered by Soxhlet extraction (using a Whatman cellulose thimble) from a weighed sample of dried (60 °C for 24 h) oil sand with refluxing toluene until the draining solvent was colorless (after approximately one hour). The bitumen solution was centrifuged to remove any suspended solids, then filtered (Whatman #1 filter paper) which also serves to absorb any residual suspended water. The solvent was

allowed to evaporate in the air-flow of a fume-hood until the bitumen reached constant weight. A small volume (~1 mL) of toluene was then re-introduced to the bitumen for viscosity reduction in preparation for subsequent isolation of the various fractions.

2.2.2. Extraction of C7A.^{15,40,41} A 40-fold excess of *n*-heptane was added to the recovered bitumen or residues pre-softened with toluene and stirred overnight. The resultant mixtures were then filtered under vacuum, to recover the precipitated C7A (designated C7A(1)). The corresponding C7M fractions were obtained from the filtrate by evaporating the solvent in air. By using this procedure, no precautions were taken to prevent possible oxidation of any fractions during solvent removal, although the solid samples were subsequently stored in the dark under nitrogen.

2.2.3. Extraction of C5A, C7A and C5-C7R. A 40-fold excess of *n*-pentane was added to the toluene-softened bitumen or residues and the mixture covered to prevent excessive solvent evaporation, and stirred overnight. The mixture was then slowly vacuum filtered (Whatman #1 filter paper) to prevent excessive evaporative cooling and recover the precipitated C5A. The C5M fractions were collected following solvent evaporation in air. Approximately half of the isolated C5A was then used to prepare C7A (designated C7A(2) in order to indicate the two-stage procedure) and C5-C7R, by suspending overnight with stirring in *n*-heptane, followed by filtering (Whatman #1 filter paper) and washing with *n*-heptane (see Fig. 1).³² The C5-C7R fractions are soluble in *n*-heptane, but insoluble in *n*-pentane.

2.2.4. Asphaltene and resin extraction from refinery asphalt. In this case, the solid asphalt, which had been received as pellets of approximate diameter 5 mm, was first ground in a mortar and pestle, and a weighed amount then placed in a Soxhlet thimble, as described for the above oil sand extraction procedure. *n*-Pentane was used as the first extraction solvent to remove *n*-pentane soluble components, although being the product from a pentane deasphalting process it was not expected to recover a significant quantity of C5M from the sample following solvent evaporation. The corresponding insoluble C5A remained in the thimble, and after solvent evaporation, the yield was calculated. After removing a known quantity of C5A, the thimble and its remaining contents were Soxhlet extracted with *n*-heptane, leaving C7A(2) as a residue in the thimble. As before, solvent removal afforded the C5-C7R fraction.

2.3. Infrared spectroscopy. Infrared spectra of the solid fractions were determined using a Brüker Alpha FTIR spectrometer (Brüker UK Ltd., Banner Lane, Coventry, UK) in attenuated total reflection (ATR) mode.

2.4. Isothermal adsorption experiments. All stock asphaltene or resin solutions were prepared by dissolving a weighed amount of the component in toluene and leaving to stand in the dark for 18 hours prior to use. As a rule, adsorption experiments were run individually, but selected examples were duplicated to verify trends in the data and found to be within the uncertainties indicated on the

plotted results. For the adsorption experiments, the required mass (m_s , ranging between 0.04–5 g) of ambient relative humidity (RH) kaolinite was weighed directly into separate 20 mL glass scintillation vials. RH was not controlled for this adsorbent, as we reported previously for sand,²⁵ although Hatch et al.³⁵ showed the water coverage to be ~1 monolayer and relatively insensitive to RH between 20–60%, typical of our experimental conditions.²⁵

Using a calibrated micropipette, 10 mL of the asphaltene solutions was slowly added to each of the vials containing the weighed kaolinite, which were then sealed with foil-lined screw caps. The vials were left to equilibrate at 23 ± 1 °C for 24 hours on a roller mixer (Stuart) which allows adequate time for adsorption equilibrium to be established (from measurements made at different times) and ensures uniform distribution of the solution and mineral particles.^{41,42} In the many adsorption studies reported in the literature, various techniques have been used to determine the concentration of dilute asphaltene solutions, with UV-visible (UV-vis) spectrophotometry being the most common,^{8,43–50} and this was used here. After equilibration, the contents of the vials were transferred to 1.5-mL polypropylene centrifuge microtubes (Axygen) and centrifuged (Sigma Laborzentrifugen 2-15 Howe centrifuge; 7 minutes at 15,000 rpm). Each supernatant solution was then transferred to a clean, dry quartz cuvette and stoppered, and its UV-vis spectrum determined (Thermo-Scientific Evolution 220 UV-vis spectrophotometer) over the wavelength range 300–800 nm (scan speed = 120 nm/min). Depending on the asphaltene solution concentration, dilution with toluene was sometimes necessary prior to recording the spectra.

Prior to the adsorption experiments, calibration plots were constructed for each of the fractions– see Supporting Information) according to the Beer-Lambert law:

$$\text{Abs} = \epsilon Cl \quad (2)$$

where Abs is the absorbance measured (at 450 nm), C is the bulk concentration of the adsorbate, l is the path-length (1 cm in this case) and ϵ is the extinction coefficient obtained from the slope of each linear plot for each fraction. Eq. 2 is used to determine the concentration depletion of the different fractions, allowing the adsorbed amounts (Γ in mg/g) to be calculated using eq. 3:

$$\Gamma = \frac{(\text{Abs}_0 - \text{Abs}_{eq})V}{1000\epsilon m_s} \quad (3)$$

where Abs_0 and Abs_{eq} are the initial and equilibrium absorbance values of the solutions and V is the solution volume.

2.5. Isotherm modeling and the solid-liquid equilibrium (SLE) model. The two main adsorption isotherm models used to explain the behavior of adsorbed asphaltene and resins in clay adsorbents have been based on the Langmuir and Freundlich adsorption isotherms,⁸ respectively producing Type I and Type III isotherms, according to the IUPAC representation.⁵¹ Acevedo et al.

have provided evidence for continuous adsorption of Hamaca asphaltenes for over 120 hours, indicating the presence of a multilayer adsorption.⁵² This type of adsorption isotherm, involving non-ideal and reversible adsorption is explained by the presence of a heterogeneous surface with non-uniform distribution of adsorption affinities, and formulated in the Freundlich isotherm model.⁵³⁻⁵⁶ However, much of the previous work reported in the literature has focused on the use of the Langmuir isotherm, based on monolayer adsorption of asphaltenes on the surface of the adsorbent.^{8,46,57-59} The main difference between the Freundlich and Langmuir adsorption isotherms is the restriction of the latter to monolayer formation.^{54,55} The Langmuir isotherm assumes that the thickness of the adsorbed layer is equivalent to one molecule, and that adsorption is dependent on the number of finite (fixed) localized sites, which in turn possesses equal affinity towards the adsorbate.^{60,61}

As outlined earlier in this paper, Guzmán et al. identified that asphaltene adsorption on nanoparticles is dependent on the experimental procedure used to determine the isotherm.³ The Type I and Type III isotherms respectively produced using methods 1 and 2, described above, were demonstrated to be well-fitted using the SLE model, originally developed by Talu and Meunier.²⁸ Derivation of the model is fully described elsewhere,^{3,28,29} and relates the equilibrium adsorbate concentration, c_e , and adsorbed amount, Γ , viz.,

$$c_e = \frac{\psi H}{1 + K\psi} \exp\left(\frac{\psi}{\Gamma_{max} A_s}\right) \quad (4)$$

where

$$\psi = \frac{-1 + \sqrt{1 + 4K\phi}}{2K} \quad (5)$$

and

$$\phi = \left(\frac{\Gamma \Gamma_{max}}{\Gamma_{max} - \Gamma}\right) A_s. \quad (6)$$

In the above equations, H is the Henry's Law constant, a measure of the relative affinity of the adsorbate for solution and surface phases (such that the lower the value of H , the higher the strength of adsorption), K is a measure of the association of adsorbate molecules on the adsorbent surface, Γ_{max} is the maximum adsorption, and A_s is the specific surface area of the adsorbent.

Following the procedure detailed elsewhere,^{3,29} Microsoft Excel Solver was used to determine the adsorption parameters H , K , Γ_{max} and A_s in eqs. 4-6 from the various isotherms. In most cases, Solver readily provided fits to the data with R^2 values better than 0.995.

3. RESULTS AND DISCUSSION

3.1. Characterization of asphaltene and resin fractions. Table 2 contains CHN elemental analyses for the

different fractions. In general, the C5-C7R fractions have a lower carbon content than the corresponding C7A fractions. The C/H ratios are therefore lower for the C5-C7R fractions than both the corresponding asphaltenes, consistent with the expectation of lower resin aromaticity. This point will be considered further in the next section. Compositional analyses for C7A(1) and C7A(2) obtained from B1 are seen in Table 2 to be similar, as would be expected. The differences that are evident can be explained by the presence of a residual C5-C7R component in C7A(2). Details of the mass compositions of C5A fractions for the four oil sources are given in Table 3.

Infrared spectra of the components are shown in Fig. 2, from which it is seen that within a fraction class each component essentially exhibits the same spectral features, irrespective of source, particularly relating to the indicated C=O, C=C and S=O bands at 1705, 1606 and 1030 cm^{-1} , respectively. Noteworthy, is the reduction in the C=C (aromatic) band and the presence of stronger S=O bands in all C5-C7R spectra; the two bitumen C5-C7R spectra show the presence of C=O bands, although the latter are absent in the asphalt and topped residue spectra. It is possible that some oxidation of susceptible species may have taken place during fraction isolation.

Table 2. Elemental composition of the fractions

Source	Fraction	Atomic composition (wt%)			C/H atomic ratio*
		C	H	N	
As1	C5A	84.84	7.71	1.16	0.92
	C7A(2)	85.37	7.47	1.16	0.95
	C5-C7R	84.84	9.17	0.66	0.77
	C5M	81.76	9.71	0.34	0.70
B1	C5A	79.56	8.15	0.98	0.82
	C7A(1)	78.37	8.08	0.95	0.82
	C7A(2)	79.87	8.21	1.02	0.82
	C5-C7R	81.76	9.71	<0.3	0.71
B2	C5A	80.39	8.02	1.11	0.84
	C7A(1)	80.55	8.04	1.13	0.84
	C5-C7R	80.75	8.62	0.78	0.79
R1	C5A	82.64	8.56	0.98	0.81
	C7A(2)	82.68	7.88	1.03	0.88
	C5-C7R	82.92	9.26	0.82	0.75

*Based on replicates of individual elemental analyses being a maximum ± 0.3 wt% (absolute), corresponding errors in the atomic ratio are in the range 0.02-0.04.

Table 3. Mass compositions of C5A fractions for the four oil sources

Source	C5A in original oil (% m/m)*	Mass fraction of C7A in C5A from two-stage preparation**	Mass fraction of C7A in C5A from UV-vis (calculation given in Supporting Information)*
As1	56.8 ± 2.8	0.74 ± 0.04	0.72 ± 0.03
B1	19.8 ± 1.0	-	0.96 ± 0.03 [C7A(1)]
		0.70 ± 0.04	0.88 ± 0.03 [C7A(2)]
B2	16.3 ± 0.8	0.91 ± 0.05	0.96 ± 0.03
R1	14.8 ± 0.7	0.75 ± 0.04	0.86 ± 0.03

* Errors of ±3% compounded from weighing and dilution.

**Errors of ±5% estimated from weighing and separation losses.

Figure 2. Infrared spectra for fractions extracted from (in descending order) B1 (black), As1 (green), R1 (blue) and B2 (red): (a) C7A; (b) C5A; and (c) C5-C7R.

3.2. Beer-Lambert plots. Absorbance versus concentration plots for all the fractions studied are linear as shown in Fig. S1 (Supporting Information) in accordance with the Beer-Lambert relationship (eq. 2), with no evidence of nonlinearity being found up to ~500 mg/L, enabling post-adsorption residual concentrations in this range to be determined.

For each of the sources, the respective extinction coefficients obtained from absorbance vs. concentration plots are generally found to decrease in the order C7A > C5A >> C5-C7R >> C5M, the latter value (for As1) confirming that the majority of aromatic species had been removed by *n*-pentane addition. This trend mirrors the respective compositional data which relate to the aromaticity of the fractions, since polycyclic aromatic hydrocarbon (PAH) chromophores are responsible for the UV absorption characteristics.⁶²⁻⁶⁴ However, we also note that very recent work⁶⁴ suggests that our selection of 450 nm as the analytical wavelength for asphaltenes may contain both absorption and scattering contributions. Notwithstanding this, Fig. 3 indicates a general trend ($R^2 = 0.9024$) in the compositional and spectroscopic results, ranging between the more highly-colored aromatic (high C/H ratio) asphaltenes and more paraffinic lower C/H ratio) resins.

Figure 3. Linear regression ($R^2 = 0.9024$) between the calibration constant (extinction coefficient) at 450 nm and the carbon/hydrogen atomic ratio for all fractions studied.

For the B1 sample, C7A(1) produced a slightly higher extinction coefficient than C7A(2), indicating more effective removal of the resin component in the single stage process. On the basis that the C5A compositions are given by eq. 1, it follows that the proportions of C7A and C5-C7R can be estimated from the respective extinction coefficients shown in Fig. S1 (Supporting Information). From the treatment also given in the Supporting Information, the mass percentages of C5-C7R in C5A vary considerably: B1 and B2 each contain ~4%; R1 contains ~14%; and As1 contains 28%. The larger values reflect the variability of feedstock (As1) as well as effects of thermal treatment (R1).

3.3. C7 asphaltene adsorption isotherms. In Fig. 4 are shown adsorption isotherms (at 23 ± 1 °C) for the C7A fractions, each of which was determined by varying the

mass of kaolinite placed in contact with 1000 mg/L toluene solutions of C7A from different sources for sufficient time to attain adsorption equilibrium. Fig. S2 (Supporting Information) shows that complete adsorption occurs within 3 h. The isotherms in Fig. 4 have been plotted in the conventional way, relating the amount adsorbed (adsorption density) to the bulk adsorbate concentration (c_e) after attainment of equilibrium, and are all very similar Type I,⁵¹ irrespective of the source. Type I isotherms such as these can generally be described using the Langmuir model (LM):

$$\Gamma = \Gamma_{max} \frac{K_L c_e}{1 + K_L c_e} \quad (7)$$

where Γ_{max} is the maximum adsorption and K_L is a constant relating to the affinity of the adsorbate for the adsorbent surface.

Fig. 4a shows that the combined adsorption data for the different C7A samples is approximated by the LM ($\Gamma_{max} = 23.7$ mg/g and $K_L = 2.40 \times 10^{-3}$ L/mg; $R^2 = 0.855$). Regression analyses for the individual component isotherms also produce relatively poor regression (R^2) coefficients with this model (Table S1, Supporting Information). Improved regression is found for most fractions at $c_o = 1000$ mg/L using the exponential Langmuir model (ELM)⁶⁵, i.e., eq. 8, with an exponent $n = 2$ and affinity constant K'_L , although noticeably poorer fits are obtained with the lower concentration c_o data for As1 (Table S2, Supporting Information).

$$\Gamma = \Gamma_{max} \frac{K'_L c_e^n}{1 + K'_L c_e^n} \quad (8)$$

However, the most consistent model that applies to this series of fractions is based on the *shifted* Langmuir model (SLM),⁶⁵

$$\Gamma = \Gamma_{max} \frac{K_s (c_e - c_s)}{1 + K_s (c_e - c_s)} \quad (9)$$

where c_s is the concentration shift and K_s the corresponding affinity constant. Eq. 9 accounts for deviations at low c_e (Table S3, Supporting Information). This is exemplified by data for As1 in Fig. 4b. A previous study involving the SLM did not identify specific reasons for a concentration shift, except insofar as c_s represents the minimum adsorbate concentration before adsorption readily occurs.⁶⁵

However, whilst the C7A data for initial asphaltene concentrations of 1000 mg/L shown in Fig. 4a appear to be in good comparative agreement from source to source, it is apparent that isotherms produced using different initial concentrations, c_o , do not overlap, as previously observed by Wang et al.²⁶ The SLM and SLE models both yield excellent fits to the data shown in Fig. 4b. As is evident from this plot, together with the SLM fitting data in Table S4 (Supporting Information), increasing c_o results in c_s and K_s both increasing, whilst Γ_{max} decreases. This suggests that the affinity between asphaltene and kaolin-

ite decreases as c_o increases. Consistent with this, the increase in H with increasing concentration found using the SLE model (Table 4) also indicates a decrease in affinity between asphaltene and the kaolinite surface, consistent with the largest value of K at a concentration of 100 mg/L, implying greater asphaltene-asphaltene association.

Figure 4. (a) Adsorption isotherms for C7A fractions from different sources for constant $c_o = 1000$ mg/L. The curve is the best-fit Langmuir model (eq. 6). (b) Adsorption isotherms for As1 C7A at three different initial concentrations, c_o . Full lines are best-fits to the shifted Langmuir model, eq. 9, and dashed lines are fitted to individual data points using the SLE model. (c) Adsorption data from (a) and (b) as a function of the asphaltene/kaolinite mass ratio. The curve is fitted to the pseudo-Langmuir equation (eq. 10), and some points are superimposed.

Table 4. Summary of SLE model adsorption parameters for C7A fractions obtained for constant initial asphaltene concentration and varying kaolinite mass.

Source	c_o (mg/L)	H (mg/g)	K (g/g)	Γ_{max} (mg/m ²)	A_s (m ² /g)	R^2
As1	1000	53.0	0.29	0.77	19.9	0.999
	500	26.5	0.18	1.08	21.1	0.999
	100	15.6	0.86	0.79	20.6	0.999
B1	1000	21.7	0.14	0.80	20.8	0.999
B2	1000	36.0	0.13	0.84	21.8	0.999
R1	1000	63.3	0.32	0.76	19.7	0.999

Also evident from the SLE model parameters in Table 4 is that the derived specific surface area, A_s , for kaolinite is ~ 20 m²/g, which is $\sim 3\times$ higher than the measured BET surface area, but consistent with the range quoted above for kaolinite based on other literature studies.³³⁻³⁹ We have no explanation for this discrepancy at the present time.

In Fig. 4c are plotted all C7A adsorption data as a function of the c_o/m_s ratio (Φ), according to Wang et al.²⁶ It can be seen that the data reduce to a single curve, which we describe here by a “pseudo-Langmuir” equation,

$$\Gamma = \Gamma_{max} \frac{K'' \Phi}{1 + K'' \Phi} \quad (10)$$

where $\Phi = C_o V / m_s \times 10^{-6}$ g/g and V is the solution volume in mL). From this equation, $\Gamma_{max} = 22.7$ mg/g and $K'' = 54.8$ ($R^2 = 0.895$).

It should be stressed that at the present time this empirical approach lacks any theoretical foundation.²⁶

3.4. C5 asphaltene adsorption isotherms. As described above for the C7A fractions, adsorption data for the corresponding C5A fractions ($c_o = 1000$ mg/L) are shown in Fig. 5. Once again, individual data for the different C5A sources are seen to be very similar. Plotted conventionally in Fig. 5a as adsorbed amount vs. c_e , the combined data are well described by the SLM using the parameters $\Gamma_{max} = 23.7$ mg/g, $K'' = 2.79 \times 10^{-3}$ L/mg and $c_s = 68.9$ mg/L ($R^2 = 0.973$). For comparison, the same data fitted with the LM yielded a regression coefficient, $R^2 = 0.819$ (see Table S1 in Supporting Information for individual analyses). It is therefore apparent that deviations from the LM is found to be greater for C5 asphaltenes, containing C5-C7R component, than the corresponding C7 asphaltenes.

Further, Fig. 5b demonstrates that the C5A data are very well-described using the pseudo-Langmuir equation (eq. 10), with $\Gamma_{max} = 20.9$ mg/g and $K'' = 56.6$ ($R^2 = 0.924$). Adsorption as measured by eq. 10 therefore appears to be only slightly different for the two sets of asphaltene frac-

tions; Γ_{max} is slightly higher for C7A, whereas K'' is slightly higher for C5A.

Figure 5. (a) Adsorption data for C5A asphaltenes from different sources for $c_o = 1000$ mg/L plotted as a function of the equilibrium bulk solution concentration. The drawn curve is the best-fit shifted Langmuir model (eq. 9). (b) The adsorption data plotted as a function of the asphaltene/kaolinite mass ratio. The drawn curve is the best-fit to the pseudo-Langmuir equation (eq. 10). Some points are superimposed.

However, comparing the SLE model parameters for the C5A fractions shown in Table 5 with the corresponding C7A values in Table 4, certain features are apparent. For example, the consistently higher H values for the C5A fractions suggest a lower affinity for the kaolinite surface than shown by the corresponding C7A fractions, whereas no systematic differences can be seen between the K values for the C5A and C7A fractions. However, the Γ_{max} values are very similar within the C5A series, irrespective of the source, and overall $\sim 10\%$ higher than the C7A series. As found for the C7A isotherms, A_s values are also approximately constant at ~ 20 m²/g. These results provide some evidence of an inhibition effect of the C5-C7R fractions on C7A adsorption, consistent with a type I resin-asphaltene association.⁶⁷ Based on resin adsorption behavior described in the following section, the resin would therefore preferentially interact with adsorption sites on the asphal-

tene, perhaps influencing asphaltene aggregation,⁶⁸ rather than competing with adsorption sites on the adsorbent.

Table 5. Summary of SLE model adsorption parameters for C5A fractions obtained for constant initial asphaltene concentration and varying kaolinite mass.

Source	c_o (mg/L)	H (mg/g)	K (g/g)	Γ_{max} (mg/m ²)	A_s (m ² /g)	R^2
As1	1000	84.4	0.30	0.92	20.0	0.999
B1	1000	65.4	0.22	0.90	19.5	0.999
B2	1000	59.0	0.16	0.90	19.6	0.999
R1	1000	72.1	0.20	0.93	20.1	0.999

3.5. C5-C7 resin adsorption isotherms. In addition to the source of the crude oil or residue, properties of most individual fractions will depend considerably on the separation procedures employed.⁶⁶ Resins are a particular case in point, since various different extraction procedures have been adopted in past studies, and these will have invariably yielded different products and potentially different conclusions. As mentioned above, the resins in this study fall into the type I classification of Navarro et al. since they precipitate with the C5A fractions.³⁹

It is immediately apparent that the adsorption isotherms shown in Fig. 6a are markedly different from those produced by the asphaltenes. All C5-C7R fractions produce typical Type III isotherms,⁵¹ which are described by a Freundlich-type equation, i.e., $\Gamma = ac_o^b$ where a and b are empirical constants. Such isotherms have been reported recently for the adsorption of *n*-heptane precipitated asphaltenes onto different high surface area synthetic nanoparticles by Guzmán et al.³ (method 2 as defined by these authors – see Introduction). Although Fig. 6 contains isotherms based on fractions obtained from different sources, the same dependence on c_o is clearly evident, for example, by comparing the isotherms for As1 at 100 and 1000 mg/L, whilst the intermediate concentration isotherms involving resins from different oil sources are also consistent with this trend. This indicates that, as found above for the asphaltene fractions, the adsorption behavior of the particular resins studied herein on kaolinite does not appear to be significantly dependent on their source.

According to Guzmán et al.,³ the dependence of the type of adsorption isotherms on the method used in their determination is indicative of adsorbate self-association (leading to dimers, trimers,...*i*-mers, nanoaggregates, clusters...), as well as interactions with the adsorbent. Similar effects were also the subject of a study by Acevedo et al. in which slow build-up of *n*-heptane-precipitated asphaltene multilayers on silica gel were identified.⁵² The point was made that in the absence of association, a single adsorption isotherm should be obtained, independent of the initial conditions (c_o , m_s).³ Indeed, the same authors further suggested that complementary results generated us-

ing experimental batch adsorption methods 1 and 2 could be used to understand interactions occurring in bulk solutions and at surfaces.³ This finding is of interest here because studies of resin association are rare. However, in one example, Castellano et al.⁶⁷ confirmed the stability of resin-resin dimers⁶⁹ based on molecular calculations structures proposed from experimental analysis. Although not as stable as asphaltene-asphaltene or asphaltene-resin pairs, the formation of van der Waals resin-resin complexes has been suggested as being viable.⁶⁷

In Fig. 6a we also show curves connecting the same mass of adsorbent used in the experiments, whilst varying c_o (i.e., method 1 of Guzmán et al.³). These latter isotherms are seen to be more typical of Type II behavior.⁵¹

Figure 6. (a) Adsorption isotherms for resins (C5-C7R) extracted from the four heavy oil/residue samples. The solid lines are drawn according to the SLE model for constant initial concentrations, c_o , whereas the dotted/dashed curves connect points for constant kaolinite mass, m_s . (b) Adsorption data plotted as a function of the resin/kaolinite mass ratio. The full curve is based on the two sets of data for the As1 fraction according to eq. 10. The inset shows the data at the lowest resin/kaolinite mass ratios.

In Fig. 6b, the adsorption data are shown as a pseudo-Langmuir isotherm, eq. 10, as a function of the resin/kaolinite mass ratio. The data are seen to become more consistent when plotted in this form. Thus the solid curve is fitted to all the data with $\Gamma_{max} = 19.8$ mg/g and $K'' = 25.0$ ($R^2 = 0.910$). With reference to the low Φ data (Fig. 6b, inset), there is an indication of a relatively small source

dependence for the resins, but the significance of this is left for future consideration. For the purposes of the present discussion, however, the similarity of the data from all sources suggests that the resins may have similar compositions. It is also apparent from the pseudo-Langmuir analysis, that adsorption of the C5-C7R fractions onto kaolinite is similar to the asphaltenes, which is not obvious from the traditional isotherms (compare Figs. 4, 5 and 6). The Γ_{max} value for the resins is seen to be comparable to the average values for the asphaltene fractions, whereas the resin K'' value is approximately half the asphaltene values.

The corresponding SLE parameters for the resins are summarized in Table 6. In comparison with the analogous asphaltene parameters in Tables 4 and 5, the resin data are most notable for the high H and K values, the former suggesting that resin-kaolinite interactions are weaker than for the asphaltenes, whilst the latter indicates that resin-resin association on the kaolinite surface is stronger than aggregation of adsorbed asphaltenes. To rationalize the form of the Type III adsorption isotherms in the case of the resins, as well as the apparent dependence on the total adsorbate/adsorbent mass ratio (Φ), the weak adsorption and strong adsorbed resin-resin interactions may promote adsorbent particle aggregation and reducing the effective adsorption capacity.

Table 6. Summary of SLE model adsorption parameters for C5-C7R fractions obtained for constant initial resin concentration and varying kaolinite mass.

Source	c_0 (mg/L)	H (mg/g)	K (g/g)	Γ_{max} (mg/m ²)	A_s (m ² /g)	R^2
As1	1000	1270.3	1.91	0.80	24.0	0.999
	100	193.5	2.75	0.61	18.3	0.962
B1	500	1333.7	3.49	0.67	14.5	0.999
B2	100	171.8	2.78	0.48	14.4	0.998
R1	300	1464.7	7.22	0.73	14.6	0.996

3.6. Adsorption models. The equilibrium adsorption of surface-active molecules on solid surfaces has been treated by Zhu and coworkers using mass action and statistical mechanics.^{70,71} However, as others have recently found, and as discussed above, asphaltene adsorption does not always appear to follow classical equilibrium adsorption models on kaolinite²⁶ and other nanoparticles.^{3,68} The former workers characterized adsorption in terms of “kinetically-limited” interactions between adsorbate and adsorbent, as found for macromolecules such as proteins. Significantly, Wang et al.²⁶ also identified a functional dependence of the adsorbed amount (of asphaltene) on the total adsorbate/adsorbent mass ratio (Φ), rather than the traditional equilibrium adsorbate concentration. Plotted as a function of Φ , our results for all three fractions exhibited similar behavior, satisfactorily fitting Langmuir-type isotherms.

On the basis of results from different batch methods (methods 1 and 2, as described in the Introduction),

Guzmán et al. proposed that two factors are responsible for the different types of adsorption behavior in their asphaltene-nanoparticle systems:³ (i) adsorbate self-association, resulting in adsorption of effectively different species, which is more applicable to method 1; and (ii) aggregation of adsorbent nanoparticles, reducing their effective adsorption capacity, and applicable to method 2. For the present systems, this behavior has been found to be characteristic of the adsorption of the resin fractions, and is summarized schematically in Fig. 7. Thus, the fact that the properties of both adsorbate and adsorbent are affected by their respective concentrations complicates the adsorption behavior and theoretical interpretations. These authors treated the results using their so-called solid-liquid equilibrium (SLE) model.^{3,29}

Figure 7. Schematic representation of the twofold effects of adsorbate (brown) and adsorbent (blue) aggregation in C5-C7R systems.

Notwithstanding the popular tenet of molecule-nanoaggregate-cluster equilibria which forms the basis of the Yen-Mullins model,^{72,73} experimental evidence also suggests that other concentration-dependent aggregated states are also present.⁷⁴ According to the latter study, asphaltene monomers exist only at very low c_0 (~5 mg/L), with dimers being formed above ~10-20 mg/L. Thereafter, further aggregation leads to the formation of nanoaggregates and larger clusters as described by the Yen-Mullins model. Inter-conversion between aggregated states is considered kinetically slow,⁷⁴ and it is therefore possible that the adsorption isotherms will be defined by the prevalent species at a given c_0 . Thus, with particular reference to Figs. 5a and 6 for C7A and C5-C7R fractions, the negligible adsorption seen below certain values of c_e may be reasonably explained by the presence of weakly-adsorbing species. In this context, Guzmán et al. attributed the appearance of Type III isotherms (as Fig. 6 herein) to adsorbent-adsorbent interactions which increase with increasing m_s , preventing effective adsorption.³ In addition, the relative similarity of adsorption data from different source oils and residues based on the same extraction procedures highlights potential limitations associated with separating the individual fractions from their parent oil environ-

ments and redissolution in toluene. The process of simplifying the system in this manner will produce a model system devoid of the interactions and complexity present in the original oil, and as shown herein, the result is a situation in which differences between the fractions from different sources show little distinction. However, it is possible that greater discrimination would arise by using mixed aliphatic/aromatic solvents (e.g., heptol), as alluded to above, or (as pointed out by a reviewer) through dynamic adsorption experiments.

The observation by Wang et al.²⁶ that concentration-dependent adsorption data become superimposable when plotted as a function of the adsorbate/adsorbent mass ratio offers a practical analysis of the present data. Each set of data relevant to the three fractions reduces to a single isotherm as described above, and summarized in Fig. 8 as pseudo-Langmuir isotherms. It should be stressed that this approach is a departure from classical theory, and as such, is not rigorous at this stage. However, it is evident from the comparison of the pseudo-Langmuir isotherms in Fig. 8, that adsorption decreases in the order C7A > C5A > C5-C7R. The presence of the resin fraction in C5A serves to explain the differences between the C5 and C7 asphaltene fractions since, in general, the resins exhibit lower surface activity. Although these conclusions could be reached by considering the traditional isotherms, the pseudo-Langmuir isotherms offer a useful approach to comparing different isotherm behaviors. Herein, we have also been able to show the similar adsorption behavior within each fraction type, irrespective of their source.

Figure 8. Pseudo-Langmuir isotherms for the three fraction types, each being averaged for the four oil sources.

4. CONCLUSIONS

In this study, we have investigated the adsorption behavior of asphaltene and resin components separated from different heavy and residual oil sources on kaolinite. The continual need to investigate the nature of the heavier polar components of crude oils arises because of the numerous operational problems that are caused by their

tendency to adsorb or deposit at surfaces during crude oil production or refinery processing.¹⁷⁻²⁰

It is appreciated that this is a simplistic approach of a highly complex system, focusing on adsorption isotherms, mostly at a single temperature. For a more complete analysis, however, it would be necessary to consider the thermodynamic aspects of the entire system, including asphaltene-asphaltene, asphaltene-resin and resin-resin interactions, together with the respective adsorption behavior on specific surfaces.

However, our results are generally consistent with those found recently by other workers on the same clay²⁶ and a range of nanoparticles,^{3,68} which strongly suggests that the adsorption behavior is sensitive to the aggregation states of both adsorbate and adsorbent.

In addition, we have found that fractions separated from four different source oils and residues using the same extraction procedures exhibit similar adsorption behavior on kaolinite. This has allowed the construction of combined adsorption isotherms based on data for the different asphaltene and resin fractions.

Following initial observations for the adsorption of asphaltenes on kaolinite,²⁶ we have rationalized the contrasting adsorption of asphaltenes (Type I) and resins (Type II/III) through the construction of “pseudo-Langmuir” isotherms by plotting adsorbed amount as a function of the adsorbate/adsorbent mass ratio. Moreover, based on the so-called SLE model, we suggest that the adsorption behavior exhibited by resins isolated from *n*-pentane-precipitated asphaltenes is a result of weak adsorption on the solid (high *H* values), combined with strong association between resin molecules on the kaolinite surfaces (high *K* values). The latter association can lead to the aggregation of adsorbent particles.

Notwithstanding the limitations of the present analysis used in this paper, we consider that this may have general applicability in systems where adsorption is found to be dependent on the concentrations and aggregated states of adsorbate and adsorbent.

ASSOCIATED CONTENT

Supporting Information. Beer-Lambert law calibration plots for the fractions (Fig. S1); Effect of adsorption time for As1 fractions (Fig. S2). Fitting parameters for the LM (Table S1), ELM (Table S2), and SLM (Table S3). This material is available free of charge via the Internet at <http://pubs.acs.org>. (PDF format)

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Notes

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ACKNOWLEDGMENTS

SET acknowledges the contribution of BP America towards the Centre for Petroleum and Surface Chemistry at the University of Surrey. The reviewers are thanked for some very constructive suggestions.

ABBREVIATIONS

C5A and C7A, asphaltenes precipitated with *n*-pentane and *n*-heptane, respectively; C5M and C7M, the corresponding maltenes fractions; C5-C7R, resin fraction insoluble in *n*-pentane and soluble in *n*-heptane; LM, the Langmuir adsorption model; RH, relative humidity; SLM, the shifted Langmuir adsorption model; SLE, solid-liquid equilibrium adsorption model; SAGD, steam-assisted gravity drainage method for bitumen production.

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