

Modeling and Prediction of Asphaltene Adsorption Isotherms Using Polanyi's Modified Theory

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ABSTRACT: The deposition of asphaltenes is one of the most difficult problems to overcome in crude oil production and processing. The presence of asphaltenes in crude oil and, consequently, the adsorption and deposition of asphaltenes on rock surfaces, affects rock properties such as porosity, permeability, and wettability. In this study, a novel model for modeling and predicting adsorption isotherms of asphaltenes based on Polanyi's modified theory is proposed. This approach enables prediction of adsorption isotherms at different temperatures (usually corresponding to reservoir temperatures), thereby improving our understanding of adsorption–equilibrium behavior at reservoir conditions, which should lead to reductions in experimental/analytical time and operation costs. The theoretical predictions of isotherms were validated successfully by determining the root-mean-square errors (RSM%) between data obtained from published literature and values predicted for asphaltenes and surfaces with differing chemical natures. The RSM% value is below 5% for all predictions. Additionally, the Dubinin–Astakhov model is used to correlate adsorption characteristic curves, resulting in RSM% values lower than 10%.

1. INTRODUCTION

Asphaltenes are high-molecular-weight constituents of heavy oil that have very complex structures and are not (yet) chemically identifiable.^{1,2} They are typically defined as the oil fraction that is insoluble in low-molecular-weight paraffins, such as *n*-heptane or *n*-pentane but soluble in light aromatic hydrocarbons, such as toluene, pyridine, or benzene.^{1,2} Regarding their structure, asphaltenes are typically formed by polyaromatic cores attached to aliphatic chains that contain heteroatoms (such as nitrogen, oxygen, and sulfur) and metals (such as vanadium, iron, and nickel).^{1–3} Therefore, asphaltenes contain polar and nonpolar groups and, consequently, exhibit amphiphilic behavior and tend to form colloidal aggregates. These colloidal aggregates are believed to significantly affect oil viscosity and specific gravity. It is well-documented that the viscosity of crude oil increases as its asphaltene content and the degree of self-association among asphaltenes increase.^{2,4–9} In addition, the polar components of asphaltene structures are likely to adsorb to the surface of the reservoir rock, which creates problems during heavy oil recovery. These problems include making the rock preferentially oil-wet, limiting crude extraction, and facilitating early depletion of the reservoir.^{2,8,10} Asphaltenes can be adsorbed on surfaces as colloidal aggregates of various sizes, or as individual molecules, by virtue of their carboxylic and phenolic weak acidic groups.^{11,12} Asphaltene adsorption onto various mineral surfaces and metal oxide nanoparticles has been reported in the literature.^{8–10,13} In general, asphaltene adsorption is studied using a batch process in which asphaltenes are extracted from heavy oil and resolubilized in a model solvent, such as toluene or Heptol (heptane + toluene). Two different types of adsorption isotherms have been reported, namely: (1) Langmuir-type

isotherms, which indicate that the asphaltene molecules form a monolayer on the solid surface,^{14–17} and (2) multisite and/or multilayer adsorption isotherms, which indicate aggregate formation and self-association of the asphaltene molecules as well as further formation of hemimicelles.^{12,16,18–20} It is noteworthy that adsorption of asphaltenes onto solid surfaces occurs due to favorable interactions between the asphaltene species and the solid surface. These favorable interactions are due to a number of interparticle forces, individually or collectively, resulting from functionalized groups (including carboxylic, pyrrolic, pyridinic, thiophenic, and sulphite) on the asphaltenes.²¹ Moreover, experimental studies regarding asphaltene adsorption behavior have limitations resulting from the complexity of asphaltene structures. The adsorption behaviors that exist in the presence of high asphaltene concentrations are complex and have not been adequately described analytically, although much has been learned about them.^{16,17} High asphaltene concentrations complicate the adsorption problem, not just due to aggregate and multilayer formation but also due to time-dependent problems and precipitation.²² Furthermore, at higher temperatures, the aggregate size of the asphaltenes decreases, significantly affecting the adsorption equilibrium.²³ If isotherms at different temperatures are desired (close to reservoir temperature), more of the adsorbate must be isolated, leading to increased experimentation time and solvent costs in addition to the experimental complexity caused by high temperatures. To avoid complexities associated with asphaltene molecules and other

Received: January 15, 2013

Revised: April 29, 2013



heavy-oil features, López-Linares et al.²⁴ have used model molecules, such as Quinolin-65 and Violanthrone-79, to mimic asphaltene-adsorption behavior. These studies have confirmed that such discrete molecules can be used to increase our understanding of asphaltene adsorption behavior. Furthermore, because adsorption of asphaltene from nonpolar and weakly polar nonaqueous solutions onto polar surfaces is largely unexplored, the nature of these processes is still not understood.²⁵

Langmuir and Freundlich adsorption isotherm models have been used previously to understand the behavior of asphaltene adsorption.^{13,26,27} However, Langmuir and Freundlich isotherm parameters provide limited insight with regard to the adsorption mechanism and nature. Alternatively, a molecular thermodynamics approach for modeling adsorption isotherms was proposed by Castro et al.²² This model was successfully used to describe and correlate equilibrium asphaltene-adsorption capacities on Berea sandstone, Bedford limestone, and dolomite rock.²² However, the model requires the determination of ten molecular parameters related to the size of the particles and the square-well potentials that describe particle–surface and particle–particle interactions in both bulk and adsorbed phases. Thus, practical use of this model is challenging and complicated.

The present study employs, for the first time, the Dubinin–Polanyi model to predict asphaltene adsorption isotherms for different surfaces of nanoparticles. The model is based on the modified Polanyi theory and, because it does not require adjustable or nonadjustable parameters, should reduce experimental time and costs. Experimental data taken from published studies were used to determine the model's accuracy. To the best of our knowledge, this is the first time that the modified Polanyi theory has been applied to complex molecules like asphaltenes. Furthermore, we propose using a correlation model based on the Dubinin–Polanyi theory to describe adsorption isotherms of asphaltenes on different solid surfaces.

2. THEORETICAL CONSIDERATIONS

The potential theory of adsorption, quantitatively formulated by Polanyi (1914),²⁸ states that, for a given adsorption system, the adsorbate potential depends on its distance to the solid surface. Assuming layer by layer coverage of adsorbent pores, equipotential surfaces are formed for each volume adsorbed. Adsorption potential is defined as the necessary work for transferring an adsorbate molecule from the adsorbent surface to a given distance. Polanyi's theory states that this potential is invariant with temperature for a given adsorption volume, as per eq 1:²⁸

$$\left(\frac{\partial A}{\partial T}\right)_{N_{\text{ads}}} = 0 \quad (1)$$

where, A is the adsorption potential (J/mol), T is the temperature (K), and N_{ads} is the adsorbed amount (mg/g).

This statement leads to an adsorption characteristic curve for each adsorbent–adsorbate system. This curve presents a relationship between adsorption potential and volume of adsorbed phase and remains independent of temperature. The temperature invariance of this characteristic curve has been previously reported for physical adsorption systems.²⁹ It is noteworthy that this model has been widely used for gas and vapor adsorption systems.^{30,31} For a gaseous adsorbate, as the pressure increases, the adsorption potential decreases until it

reaches saturation pressure, at which point a liquid layer forms on the solid surface. The adsorption potential for a gaseous adsorbate in/on a specific equipotential surface can be described mathematically as follows:^{30,31}

$$A = RT \ln\left(\frac{P_s}{P}\right) \quad (2)$$

where, P_s is the saturation pressure (atm), P is the equilibrium pressure (atm), T is the temperature (K), and R is the ideal gas universal constant (J/(mol K)). Although Polanyi's theory was originally used to describe gas/vapor adsorption on porous materials, it has recently been used to describe adsorption phenomena occurring in aqueous solutions.^{32–35} On the basis of the previous treatment of gas/vapor adsorption, the aqueous-solution adsorption potential has been modified as described below.

2.1. S Model (Solubility Normalized Model). The solubility normalized model (S model) has been extensively used to describe adsorption of different contaminants from wastewater onto solid surfaces; one such example is the adsorption onto biomass of organic compounds and cations, and ion-exchange onto zeolite.^{32,36} In this case, the adsorption potential for aqueous solutes, in which solid precipitation replaces gas condensation, is defined as follows:³⁶

$$A = RT \ln\left(\frac{C_s}{C}\right) \quad (3)$$

where C_s is the adsorbate solubility in the solvent used (mg/L) and C is the equilibrium concentration (mg/L). Therefore, to use the S model, the adsorbate solubility at a given temperature must be known. The simplified Flory–Huggins theory has been proposed to estimating the asphaltene solubility in toluene (for asphaltene–toluene solutions). Assuming that asphaltenes are monodisperse polymeric molecules, the theory states³⁷

$$C_s = 100 \times \exp\left[\frac{V_A}{V_T} - 1 - \frac{V_A}{RT}(\delta_A - \delta_T)^2\right] \quad (4)$$

where, V_A and V_T are the molar volumes (m³/mol) of asphaltenes and toluene, respectively, and δ_A and δ_T are the solubility parameters (Pa^{0.5}) of asphaltenes and toluene, respectively. This model assumes that the asphaltene flocculation process is reversible. It should be noted that solubility parameters depends on the molecular weights of both the solute and the solvent. Although the properties of toluene are well-known, the properties of asphaltenes are more complex, and, as a result, the molecular mass of asphaltene is unsolved or debatable. To estimate the molar volumes and solubility parameters of the adsorption process, we use the asphaltene molecular mass and density that have been reported in the literature (750 g/mol and 1280 g/L, respectively).¹³ Accordingly, the asphaltene solubility parameter estimated by fitting the experimental data to the model equals 1.75 MPa^{0.5}. Asphaltene solubility in toluene was estimated to be 34, 46.8, 62.5, and 81.3 mg/L at 25, 40, 55, and 70 °C, respectively.

2.2. C Model (Non-normalized Model). The C model (empirical model) represents another expression for Polanyi's adsorption potential and has been proposed to describe the adsorption of polycyclic molecules, such as dyes.³³ Thus, the model is expected to be applicable to asphaltene adsorption. The adsorption potential is estimated as follows:

$$A = RT \ln \left(1 + \frac{1}{C} \right) \quad (5)$$

where the units of C are grams solute per gram solvent. This empirically based expression does not require knowledge of any solution property; however, this expression, unlike the S model, has no theoretical basis. Nonetheless, this non-normalized model has been used successfully to estimate/describe adsorption of metal ions and dyes from aqueous solutions onto different adsorbents.³²

2.3. Dubinin–Astakhov Model. To obtain a thermodynamic model for adsorption, Dubinin and Astakhov (1971) developed the following model on the basis of S or C models and Weibull statistic distribution:³³

$$N_{\text{ads}} = N_{\text{ads,max}} \exp \left[- \left(\frac{A}{E} \right)^n \right] \quad (6)$$

where N_{ads} is the adsorbed amount (mg/g) at equilibrium, $N_{\text{ads,max}}$ is the maximum adsorbed amount (mg/g), A is the adsorption potential estimated by the C model or the S model, and E and n are distribution parameters obtained from characteristic curves and represent adsorption energy and surface heterogeneity, respectively. It should be noted that A , E , and n (in eq 6) are temperature independent. The Dubinin–Astakhov model has been used successfully to describe the adsorption of dyes from aqueous solution.^{32,36} In the present study, this model has been extended for the first time to asphaltene adsorption onto different solid surfaces.

The heterogeneity parameter n is expected to mostly depend on adsorbent structure, but it also depends, to a lesser extent, on adsorbate properties.^{38,39} This parameter increases for homogeneous adsorbent surfaces. The typical value of n for activated carbon is 2, while the typical value for zeolite is 4.^{32,36} The adsorption energy E increases as additional interactions take place at the adsorbent surface.³² The model parameters are obtained by minimizing the error between theoretical (S or C model) and experimental data points. Toward this end, the error definition used was the root-mean-square error (RMS%), determined via eq 7. The calculated error values are given in Table 1

$$\text{RSM\%} = 100 \sqrt{\frac{1}{k} \left[\sum_{i=1}^k \left(\frac{C_{\text{exp}} - C_{\text{cal}}}{C_{\text{cal}}} \right)^2 \right]} \quad (7)$$

Table 1. Root Mean Square Percent Error (RSM%) Values Calculated for the Prediction Models

model	adsorbent	RSM%			ref
		40 °C	55 °C	70 °C	
C	γ -Al ₂ O ₃ nanop	4.40	5.02		Nassar ¹³
	Si nanop	1.03	3.66	3.08	Cortés et al. ²⁶
	SNi15 nanop	2.48	4.88	2.83	Cortés et al. ²⁶
	Al nanop	1.08	0.78	2.70	Franco et al. ²⁷
	AlNi15 nanop	2.58	2.51	3.86	Franco et al. ²⁷
S	γ -Al ₂ O ₃ nanop.	5.59	5.69		Nassar ¹³
	Si nanop	3.92	5.31	5.06	Cortés et al. ²⁶
	SNi15 nanop	4.70	5.35	5.21	Cortés et al. ²⁶
	Al nanop	3.16	1.75	0.80	Franco et al. ²⁷
	AlNi15 nanop	3.13	5.49	4.92	Franco et al. ²⁷

3. METHODOLOGY FOR MODEL FITTING AND PREDICTION

To construct adsorption isotherms at different temperatures, the first step is to obtain experimental data (for adsorption isotherms) at a known temperature (i.e., C_o , N_{ads}), where C_o is the concentration at equilibrium in milligrams per liter and N_{ads} is the adsorbed amount in milligrams per gram. Polanyi postulated that N_{ads} remains constant for different temperatures. Therefore, equilibrium concentrations at different temperatures can be estimated using the adsorption potential from eq 3 (S model), as follows:

$$RT \ln \left(\frac{C_s}{C} \right) = RT_o \ln \left(\frac{C_{so}}{C_o} \right) \quad (8)$$

where, C_o , C_{so} , and T_o are the experimental isotherm conditions and C and C_s are the predicted isotherm conditions. Thus, because the only unknown variable is C , the equation can be reorganized, and C can be computed. For the C model, the procedure is the same. The equations obtained are shown below.

S model

$$\ln C = \ln C_s - \frac{T_o}{T} \ln \left(\frac{C_{so}}{C_o} \right) \quad (9)$$

C model

$$C = \frac{1}{\left[\exp \left(\frac{T_o}{T} \right) \left(1 + \frac{1}{C_o} \right) \right] - 1} \quad (10)$$

Finally, new isotherms can be constructed by plotting N_{ads} against C , using the calculated concentrations and N_{ads} calculated in the experimental isotherm.

4. RESULTS AND DISCUSSION

Figures 1a–c show the experimental data obtained by Nassar¹³ together with S and C model fits for Athabasca C7-asphaltene adsorption onto γ -Al₂O₃ nanoparticles at different temperatures. Clearly, there is excellent agreement between the model and experimental results. It is worth noting that the isotherm curves in Figures 1b and c are model predictions. Both S and C models predicted the experimental data excellently, with RSM% values lower than 5.69. Due to its theoretical basis, we expected the S model to provide a better fit than the C model. However, the empirical C model appears to bear more resemblance to the experimental data. This unanticipated outcome could be attributed to the fact that the S model requires calculation of the asphaltene solubility at the given temperature. As mentioned above, adsorbent solubility is an important parameter in the S model and is strongly dependent on solute and solvent molecular weights and interactions. The asphaltene molecular weight depends on several factors, including the type of crude oil being analyzed, the solvent used for extraction and dissolution as well as the temperature. Furthermore, the tendency of asphaltenes to form aggregates hinders molecular-weight determination.^{35,36} All these factors mean that the asphaltene solubility in toluene is an adjustable parameter, and this condition brings uncertainty to the S model. Additionally, the C model is particularly suited for describing the adsorption of polycyclic molecules,³³ such as the molecular structure of asphaltenes.

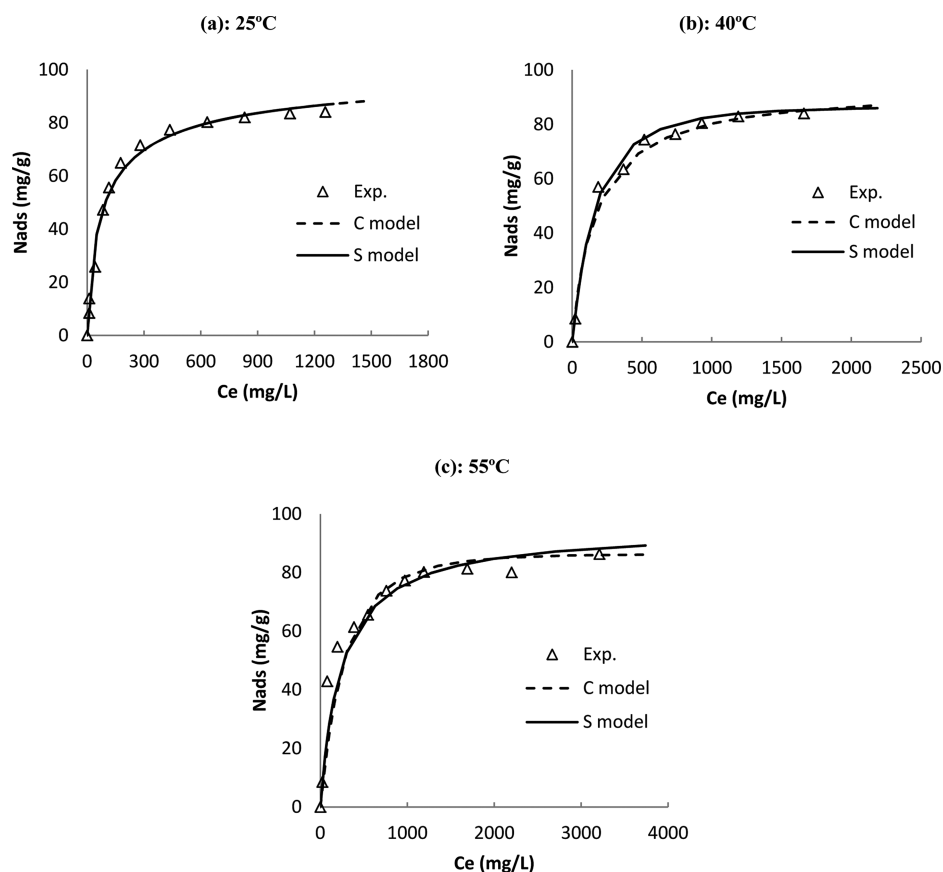


Figure 1. Isotherms of asphaltene adsorption onto γ - Al_2O_3 nanoparticles at (a) 25, (b) 40, and (c) 55 °C. The symbols are experimental data obtained from Nassar,¹³ and the solid and dashed lines are from eqs 9 and 10, respectively. Lines in plot a represent the modeled fit, while those in plots b and c represent model predictions.

Table 1 shows the RSM% values for C- and S-model predictions of asphaltene adsorption onto different surfaces at different temperatures. In all cases, the RSM% values are lower than 5.69, indicating good agreement between the experimental data and the model. This demonstrates the accuracy and applicability of these Polanyi-based models (C- and S-model) to asphaltene adsorption. It is worth noting here that asphaltene adsorption is influenced by intermolecular forces between the asphaltene molecules and the solid surface. Asphaltenes can exhibit a wide variety of molecular structures, which results in more complex and varied aggregates (due to various interactions that can occur).^{13,40–44} Depending on the solvent, the nature or origin of the asphaltenes, and the experimental conditions, different types of aggregates have been reported.^{13,40–44} The sizes and shapes of these aggregates are strongly affected by temperature. It is plain to see that asphaltene adsorption onto solid surfaces is a complex process; consequently, predicting the resulting adsorption behavior is complicated and requires special attention. Nonetheless, the S and C models employed in this study are capable of accurately predicting asphaltene adsorption.

Figure 2a–g shows the characteristic curves for asphaltene adsorption onto different surfaces of nanoparticles. In all cases, as the amount of adsorbed asphaltenes increased, the adsorption potential decreased until it leveled off at a maximum capacity corresponding to monolayer coverage. This is in total agreement with the monolayer coverage of Langmuir type-I adsorption reported by Nassar,¹³ suggesting that it requires more energy for asphaltene molecules closer to the adsorbent

surface to desorb. The adsorption system exhibits temperature invariance (i.e., for different temperatures, the data points are described by a characteristic curve), indicating that the adsorption taking place is physical. The characteristic curve is correlated with Dubinin–Astakhov’s model, and the values of the obtained model parameters and their corresponding RSM% values are presented in Table 2. Dubinin–Astakhov’s model correlates accurately with the characteristic curve-points computed by both models (C- and S-model), indicating that the parameters obtained precisely represent the adsorbate–adsorbent system. Further, as seen in Table 2, the D–A model parameters are adsorbent-specific. These differences in the values of D–A parameters could be attributed to the different degree of interaction between the asphaltene molecules and the adsorbent surface.⁴⁶

The D–A and Polanyi models are based on adsorption potential rather than physical mechanisms. Thus, the models are global to predict and correlate different adsorption behavior. For further understanding of asphaltene adsorption mechanisms onto different materials, experimental data were fitted to Langmuir and Freundlich models. The resulting correlation coefficients and RSM% are presented in Table 3. These results indicate that asphaltenes form a monolayer onto the adsorbent, and adsorption potential is the same across the surface. It is worth noting that, for asphaltene adsorption onto different materials and according to results presented in Table 3, the D–A model correlates better to the experimental data than the Langmuir isotherms model. The RSM% values obtained from the D–A model are lower than those obtained for Langmuir

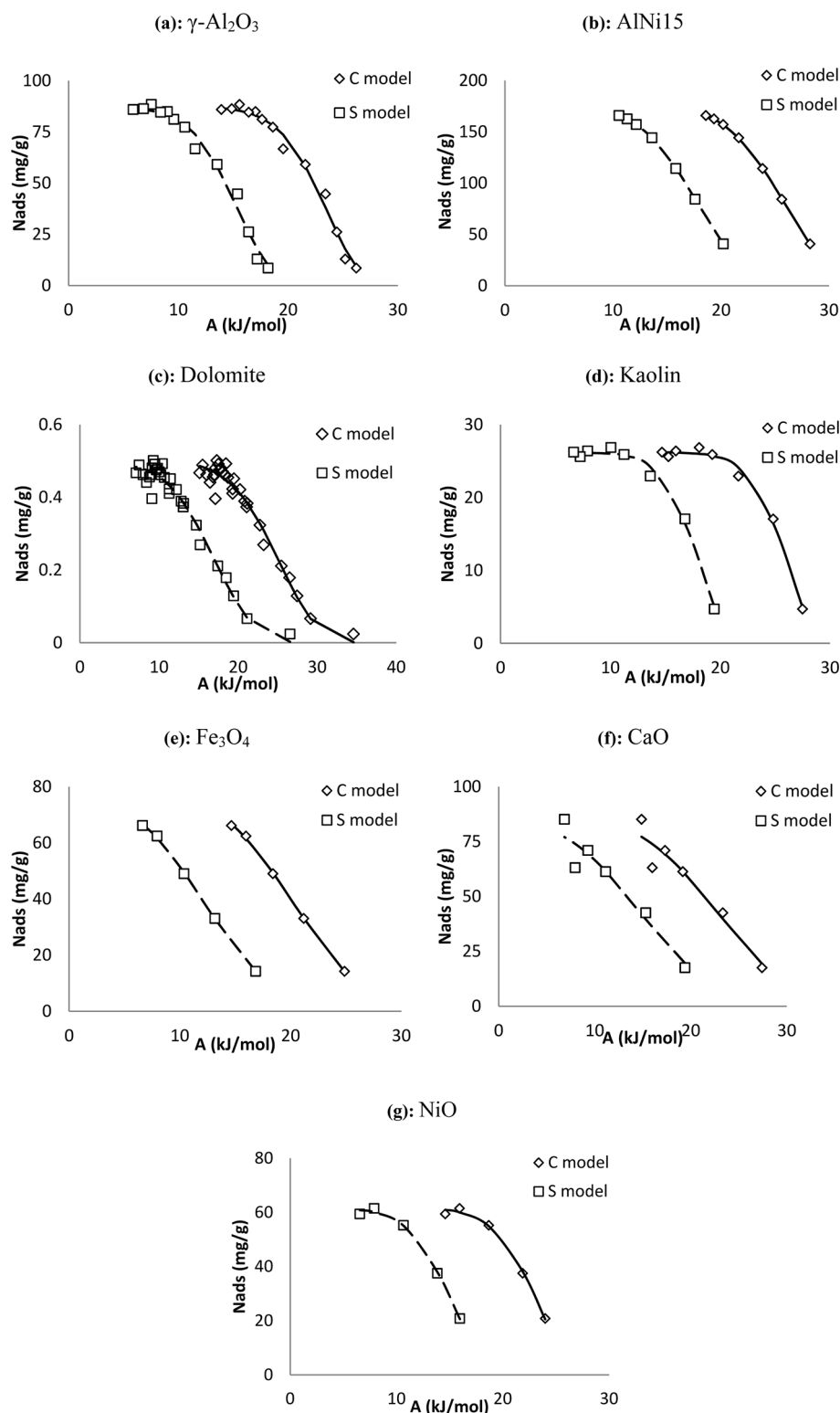


Figure 2. Characteristic curves for asphaltene adsorption onto (a) $\gamma\text{-Al}_2\text{O}_3$ nanoparticles,¹³ (b) AlNi15 nanoparticles,²⁷ (c) Dolomite sand,³⁸ (d) Kaolin powder,⁴⁵ (e) Fe_3O_4 nanoparticles,⁴⁶ (f) CaO nanoparticles,⁴⁶ and (g) NiO nanoparticles.⁴⁶ The symbols are experimental data, where A is computed from eqs 3 (\square) and 5 (\diamond); and the solid and dashed lines are from eq 6.

and/or Freundlich models. Furthermore, in the case of porous adsorbents, the D–A model suggests that asphaltenes adsorb via micropore volume filling as opposed to layer-by-layer adsorption on pore walls.³² Although, for our case the adsorbents are nonporous and the D–A model used is based on the micropore volume filling. It is worth noting here that the

Polanyi theory assumes that for a molecule located within the attractive force field of a solid, there exists an (attractive) adsorption potential (A) between the molecule and the solid surface. This an assumption of layer-by-layer coverage of the surfaces with the formation of adsorption film having an equipotential interface of the adsorption phase. Such an

Table 2. Dubinin–Astakhov Model Parameters for Asphaltene Adsorption onto Different Adsorbents

model	adsorbent	$N_{\text{ads,max}}$ (mg/g)	E (kJ/mol)	n	RSM%	R^2	ref
C	$\gamma\text{-Al}_2\text{O}_3$ nanop	87.36	23.91	8.80	3.97	0.99	Nassar ¹³
	AlNi15 nanop	180.16	26.68	7.07	0.55	0.99	Franco et al. ²⁷
	Dolomite sand	0.50	26.05	6.31	5.65	0.97	Piro et al. ³⁸
	Kaolin powder	26.22	26.40	12.50	3.22	0.99	Dubey et al. ⁴⁵
	Fe_3O_4 nanop	80.61	21.78	4.20	0.93	0.99	Nassar et al. ⁴⁶
	CaO nanop	87.77	24.75	4.03	8.77	0.93	Nassar et al. ⁴⁶
	NiO nanop	61.72	23.73	8.96	1.90	0.99	Nassar et al. ⁴⁶
	$\gamma\text{-Al}_2\text{O}_3$ nanop	86.50	15.87	5.75	5.14	0.99	Nassar ¹³
S	AlNi15 nanop	176.13	18.72	5.01	0.28	0.99	Franco et al. ²⁷
	Dolomite sand	0.49	18.08	4.34	5.60	0.97	Piro et al. ³⁸
	Kaolin powder	26.16	18.37	8.57	3.56	0.99	Dubey et al. ⁴⁵
	Fe_3O_4 nanop	74.65	14.13	2.87	0.76	0.99	Nassar et al. ⁴⁶
	CaO nanop	83.24	17.02	2.81	9.15	0.93	Nassar et al. ⁴⁶
	NiO nanop	61.19	15.73	5.78	1.65	0.99	Nassar et al. ⁴⁶

Table 3. Correlation Coefficients and RSM% Values for Dubinin–Astakhov, Langmuir, and Freundlich Models for Different Adsorption Systems

adsorbent	correlation coefficient (R^2)			RSM%			ref
	D–A (C model)	Langmuir	Freundlich	D–A (C model)	Langmuir	Freundlich	
$\gamma\text{-Al}_2\text{O}_3$ nanop	0.99	0.99	0.86	3.97	10.14	16.18	Nassar ¹³
AlNi15 nanop	0.99	0.99	0.92	0.55	0.97	15.31	Franco et al. ²⁶
Dolomite sand	0.97	0.99	0.85	5.15	5.24	15.12	Piro et al. ³⁸
Kaolin powder	0.99	0.99	0.68	3.22	2.77	13.62	Dubey et al. ⁴⁵
Fe_3O_4 nanop	0.99	0.99	0.96	0.93	2.95	6.58	Nassar et al. ⁴⁶
CaO nanop	0.93	0.96	0.90	8.77	9.57	10.11	Nassar et al. ⁴⁶
NiO nanop	0.99	0.99	0.83	1.90	9.41	16.73	Nassar et al. ⁴⁶

approximate assumption could be justified for adsorption on nonporous or large-pore adsorbents when polymolecular adsorption films representing adsorption phases are formed. In this case, the modified D–A model have been developed by two ways: (1) employing the adsorption potential (A) and (2) employing the theory of the volume filling of micropores (TVFM). The results found in our study show that this model can represent the adsorption behavior of asphaltenes on nonporous materials with very good fit using the D–A model. We think that in our study the potential theory is more important than TVFM, and for this reason the D–A model shows good fit results for the nonporous–asphaltene pair. Consequently, the D–A model can be used for describing the asphaltene adsorption on nonporous materials. This theory is based on Polanyi which permits prediction and models the adsorption behavior of asphaltene on macropores.

5. CONCLUSIONS

Asphaltene adsorption isotherms at different temperatures could be modeled and predicted using a new model based on the modified Polanyi’s theory and without the need for intensive parameters. The resulting adsorption characteristic curves could be correlated well with the Dubinin–Astakhov model. Thus, we conclude that this model is suitable for predicting adsorption phenomena at reservoir temperatures without requiring additional experiments and can, therefore, minimize cost and time.

The model accurately described the experimental data regarding asphaltene adsorption onto different solid surfaces at different temperatures. Additionally, the study found that the experimental data obtained for asphaltene adsorption fit the

Dubinin–Astakhov model better than the commonly used Langmuir and Freundlich models.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The author Farid B. Cortés is thankful to the Prof. Farid Chejne for teaching. The authors are grateful to COLCIENCIAS, Universidad Nacional de Colombia, for logistical and financial support.

REFERENCES

- (1) Acevedo, S.; Castillo, J.; Fernandez, A.; Goncalves, S.; Ranaudo, M. Study of Multilayer Adsorption of Asphaltenes on Glass Surface by Photothermal Surface Deformation. Relation of this Adsorption to Aggregate Formation in Solution. *Energy Fuels* **1998**, *12*, 386–390.
- (2) Mousavi-Dehghani, S.; Riazzi, M.; Vafaie-Sefti, M.; Mansoori, G. An analysis of methods for determination of onsets of asphaltene phase separations. *J. Pet. Sci. Eng.* **2004**, *42*, 145–156.
- (3) McLean, J.; Kilpatrick, P. J. Effects of Asphaltene Solvency on Stability of Water-in-Crude-Oil Emulsions. *J. Colloid Interface Sci.* **1997**, *189* (2), 242–253.
- (4) Bockrath, B. C.; LaCount, R. B.; Noceti, R. P. Coal-derived asphaltenes: effect of phenol content and molecular weight on viscosity of solutions. *Fuel* **1980**, *59*, 621–626.
- (5) Rosales, S.; Machín, I.; Sánchez, M.; Rivas, G.; Ruette, F. Theoretical modeling of molecular interactions of iron with asphaltenes from heavy crude oil. *J. Mol. Catal. A: Chem.* **2006**, *246*, 146–153.

- (6) Wargadalam, V. J.; Norinaga, K.; Iino, M. Size and shape of a coal asphaltene studied by viscosity and diffusion coefficient measurements. *Fuel* **2002**, *81*, 1403–1407.
- (7) Sheu, E. Y.; Shields, M. B.; Storm, D. A. Viscosity of base-treated asphaltene solutions. *Fuel* **1994**, *73*, 1766–1771.
- (8) Mendoza, J.; Castellanos, I.; Ortiz, A.; Buenrostro, E.; Durán, C.; López, S. Study of monolayer to multilayer adsorption of asphaltenes on reservoir rock minerals. *J. Colloids Surf. A: Physicochem. Eng. Aspects* **2009**, *340*, 149–154.
- (9) Dudášová, D.; Simon, S.; Hemmingsen, P.; Sjöblom, M. Study of asphaltenes adsorption onto different minerals and clays. Part 1. Experimental adsorption with UV depletion detection. *J. Colloids Surf. A: Physicochem. Eng. Aspects* **2008**, *317*, 1–9.
- (10) Marczewski, A. W.; Szymula, M. Adsorption of asphaltenes from Toluene on Quartz and Silica-rich Soils. *Annales UMCS, Sec. AA* **2003**, *LVIII*, 69–79.
- (11) Chianelli, R. R.; Siadati, M.; Mehta, A.; Pople, J.; Ortega, L. C.; Chiang, L. Y. *Self-Assembly of Asphaltene Aggregates: Synchrotron, Simulation and Chemical Modelling Techniques Applied to Problems in the Structure and Reactivity of Asphaltenes*, in *Asphaltenes, Heavy Oils, and Petroleum*; Mullins, O. C., Sheu, E. Y., Hammami, A., Marshall, A. G., Eds.; Springer: New York, 2007; pp 375–400.
- (12) Acevedo, S.; Ranaudo, M. A.; García, C.; Castillo, J.; Fernández, A.; Caetano, M.; Goncalves, S. Importance of Asphaltene Aggregation in Determining the Adsorption of This Sample on Mineral Surfaces. *J. Colloids Surf. A: Physicochem. Eng. Aspects* **2000**, *166*, 145–152.
- (13) Nassar, N. Asphaltene adsorption onto alumina nanoparticles: kinetics and thermodynamic studies. *Energy Fuels* **2010**, *24*, 4116–4122.
- (14) Marlow, B. J.; Sresty, G. C.; Hughes, R. D.; Mahajan, O. P. Colloidal stabilization of clays by asphaltenes in hydrocarbon media. *Colloids Surf.* **1987**, *24*, 283–297.
- (15) Saada, A.; Siffert, B.; Papirer, E. J. Comparisson of the hydrophilicity/ hydrophobicity of illites and kaolinites. *J. Colloid Interface Sci.* **1995**, *174*, 185–190.
- (16) González, G.; Moreira, M. B. C. The wettability of mineral surfaces containing adsorbed asphaltenes. *Colloids Surf.* **1991**, *58*, 293–302.
- (17) Gaboriau, H.; Saada, A. Influence of heavy organic pollutants of anthropic origin on PAH retention by kaolinite. *Chemosphere* **2001**, *44*, 1633–1639.
- (18) Marczewski, A. W.; Szymula, M. Adsorption of Asphaltene from Toluene on Mineral Surface. *Colloids Surf., A* **2002**, *208*, 259–266.
- (19) Szymula, M.; Marczewski, A. W. Adsorption of Asphaltenes from Toluene on Typical Soils of Lublin Region. *Appl. Surf. Sci.* **2002**, *196*, 301–311.
- (20) Pernyeszi, T.; Patzkó, Á.; Berkesi, O.; Dékány, I. Asphaltene adsorption on clays and crude oil reservoir rocks. *Colloids Surf., A* **1998**, *137*, 373–384.
- (21) Groenzin, H.; Mullins, O. C. Molecular Size and Structure of Asphaltenes from Various Sources. *Energy Fuels* **2000**, *14*, 677–684.
- (22) Castro, M.; Mendoza de la Cruz, J. L.; Buenrostro-Gonzalez, E.; López-Ramírez, S.; Gil-Villegas, A. Predicting adsorption isotherms of asphaltenes in porous materials. *Fluid Phase Equilib.* **2009**, *286* (2), 113–119.
- (23) da Silva Ramos, A. C.; Haraguchi, L.; Notrispe, F. R.; Loh, W.; Mohamed, R. S. Interfacial and colloidal behavior of asphaltenes obtained from Brazilian crude Oils. *J. Pet. Sci. Eng.* **2001**, *32*, 201–216.
- (24) López-Linares, F.; Carbognani, L.; González, M. F.; Sosa-Stull, C.; Figueras, M.; Pereira-Almao, P. Quinolin-65 and Violanthrone-79 as Model Molecules for the Kinetics of the Adsorption of C7 Athabasca Asphaltene on Macroporous Solid Surfaces. *Energy Fuels* **2006**, *20*, 2748–2750.
- (25) Marczewski, A. W.; Szymula, M. Adsorption of asphaltenes from toluene on typical soils of Lublin región. *Colloids Surf. A: Physicochem. Eng. Aspects* **2002**, *208*, 259–261.
- (26) Cortés, F. B.; Mejía, J. M.; Ruiz, M. A.; Benjumea, P.; Riffel, D. B. Sorption of asphaltenes onto Nanoparticles of Nickel Oxide Supported on Nanoparticulated Silica Gel. *Energy Fuels* **2012**, *26*, 1725–1730.
- (27) Franco, C.; Patiño, E.; Ruiz, M. A.; Benjumea, P.; Cortés, F. B. Kinetic and thermodynamic equilibrium of asphaltenes sorption onto nanoparticles of nickel oxide supported on nanoparticulated alumina. *Fuel* **2012**, *105*, 408–414.
- (28) Polanyi, M. Verhandel. *Deut. Physik. Gee.* **1914**, *16*, 1012.
- (29) Dubinin, M. M. *Physical Adsorption of Gases and Vapors in Micropores*; Academic Press: Moscow, USSR, 1975.
- (30) Polanyi, M. Theories of the adsorption of gases. A general survey and some additional remarks. *Trans. Faraday Soc.* **1932**, *28*, 316–333.
- (31) Manes, M.; Hofer, J. E. Application of the Polanyi Adsorption Potential Theory to Adsorption from Solution on Activated Carbon. *J. Phys. Chem.* **1969**, *73* (3), 584.
- (32) Inglezakis, V. J. Solubility-normalized Dubinin-Astakhov adsorption isotherm for ion-exchange systems. *Microporous Mesoporous Mater.* **2007**, *103*, 72–81.
- (33) Inglezakis, V. J.; Stylianou, M.; Loizidou, M. Ion Exchange and adsorption equilibrium studies on clinoptilolite, bentonite and vermiculite. *J. Phys. Chem. Solids* **2010**, *71*, 279–284.
- (34) Long, C.; Li, A.; Wu, H.; Liu, F.; Zhang, Q. Polanyi-based models for the adsorption of naphthalene from aqueous solutions onto nonpolar polymeric adsorbents. *J. Colloid Interface Sci.* **2008**, *319*, 12–18.
- (35) Fuller, M.; Smith, J. A.; Burns, S. E. Sorption of nonionic organic solutes from water to tetraalkylammonium bentonites: Mechanistic considerations and application of the Polanyi–Manes potential theory. *J. Colloid Interface Sci.* **2007**, *313*, 405–413.
- (36) Cortés, F. B.; Chejne, F. A rapid and novel approach for predicting water sorption isotherms and isosteric heats of different meat types. *Meat Sci.* **2010**, *86* (4), 921–925.
- (37) Prausnitz, J. M.; Lichtenthaler, R. N.; Gomes de Azevedo, E. *Termodinámica Molecular de los Equilibrios de Fases*; Prentice Hall: Iberia, 2000.
- (38) Piro, G.; Canonico, L. B.; Galbariggi, G.; Bertero, L.; Carniani, C. Asphaltene Adsorption onto Formation Rock: An Approach to Asphaltene Formation Damage Prevention. *SPE Prod. Facil.* **1996**, *11* (3), 156–160.
- (39) Fryer, J. F.; Speight, J. G. Investigation of asphaltene molecular weights. *Fuel* **1976**, *55* (3), 227–232.
- (40) Tanaka, R.; Sato, E.; Hunt, J. E.; Winans, R. E.; Sato, S.; Takanohashi, T. Characterization of asphaltene aggregates using X-ray diffraction and small-angle X-ray scattering. *Energy Fuels* **2004**, *18*, 1118–1125.
- (41) Strausz, O. P.; Lown, E. M. *The Chemistry of Alberta Oil Sands Bitumens and Heavy Oils*; Alberta Energy Research Institute: Calgary, Alberta, Canada, 2003.
- (42) Strausz, O. P.; Peng, P.; Murgich, J. About Colloidal Nature of Asphaltene and the MW of Covalent Monomeric Units. *Energy Fuels* **2002**, *16*, 809–822.
- (43) Sheu, E. Y.; Mullins, O. C. *Asphaltenes: fundamentals and applications*; Plenum Press: New York, 1995.
- (44) Tanaka, R.; Hunt, J. E.; Winans, R. E.; Thiyagarajan, P.; Sato, S.; Takanohashi, T. Aggregates structure analysis of petroleum asphaltenes with small-angle neutron scattering. *Energy Fuels* **2003**, *17*, 127–134.
- (45) Dubey, S. T.; Waxman, M. H. Asphaltene Adsorption and Desorption From Mineral surfaces. *SPE Reservoir Eng.* **1995**, *6* (3), 389–395.
- (46) Nassar, N. N.; Hassan, A.; Pereira-Almao, P. Metal Oxide Nanoparticles for Asphaltene Adsorption and Oxidation. *Energy Fuels* **2011**, *25* (3), 1017–1023.