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# Non-linear adsorption modeling of fatty esters and oleic estolide esters via boundary lubrication coefficient of friction measurements☆

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**Abstract**

The frictional behaviors of a variety of fatty esters (methyl oleate (MO), methyl palmitate (MP), methyl laurate (ML), and 2-ethylhexyl oleate (EHO)) and oleic estolide esters (methyl oleic estolide ester (ME) and 2-ethylhexyl oleic estolide ester (EHE)) as additives in hexadecane have been examined in a boundary lubrication test regime using steel contacts. Critical additive concentrations were defined and used to perform novel and simple Langmuir analyses that provide an order of adsorption energies: EHE ≥ ME > EHO > MP > MO ≥ ML. Application of Langmuir, Temkin, and Frumkin–Fowler–Guggenheim (FFG) adsorption models via non-linear fitting demonstrates the necessary inclusion of cooperative effects in the applied model. Fits of the steady-state coefficient of friction (COF)-concentration data for EHE, ME, and EHO indicate slight cooperative adsorption. MO, MP, and ML data require larger attractive interaction terms ($\alpha \leq -2.3$) to be adequately fit. Primary adsorption energies calculated via a general adsorption model are necessarily decreased while total adsorption energies correlate well with values obtained via critical concentration analyses. To account for multiple surface-site coverage a multiple-site model was defined. The intuitive assumption of multiple-site coverage of more massive components suggests deceptively increased calculated adsorption energies for typically applied models (e.g. FFG, Langmuir).
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## 1. Introduction

As part of our effort to develop new bio-based lubricants, members of our lab have sought to characterize a wide range of bio-based materials [1,2]. Biresaw et al. previously examined a series of natural oils and methyl ester control systems as lubricant additives in a boundary lubrication test regime (Ball-on-Disk). Critical to their performance in hexadecane is their ability to adsorb to a steel surface. To characterize such systems, Jahanmir and Beltzer previously noted the ability to obtain coefficient of friction (COF)-derived adsorption isotherms [3]. Subsequently, adsorption energies may be obtained via fits to a variety of adsorption models (e.g. Langmuir, Temkin, FFG). In our previous work we noted the non-Langmuirian behavior of methyl fatty ester control systems (methyl stearate, methyl oleate (MO), methyl palmitate (MP), methyl laurate (ML)) and applied non-linear fitting and a general adsorption model [4]. In this paper we extend that work to include more complex estolide esters (methyl oleic estolide ester (ME), 2-ethylhexyl oleic estolide ester (EHE)) and an additional ester control system (2-ethylhexyl oleate (EHO)). Estolide esters display good pour points, viscosities, and oxidative stability and are thus suitable choices for bio-based lubricants [5,6]. Additionally, these oligomeric systems provide more complex surface interactions for which the theoretical models may be tested and developed. For each of the additives discussed here a cooperative adsorption model is required to adequately fit the data. The analyses of

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the oligomeric systems indicate the necessary consideration of multiple-site coverage and/or adsorption due to mass or chemical functionality of each additive.

Although commonly applied to data obtained for two-component solutions exposed to complex surfaces, the Langmuir adsorption isotherm was derived for the adsorption of ideal gases to a uniform surface [7]. This may be understood in the context of a common first-order equilibrium reaction:

$$A + B \underset{k_b}{\overset{k_a}{\rightleftharpoons}} C \tag{1}$$

$A$ is the concentration of unoccupied surface sites (adsorbent), $B$ the concentration of adsorpt (un-bound additive) and $C$ is the concentration of adsorbate (bound additive/occupied sites). The equilibrium constant $K$ ($k_a/k_b$) may be defined by both the equilibrium equation and the Arrhenius equation, respectively:

$$K = \frac{C}{AB} = e^{-E_{ads}/RT} \tag{2}$$

$E_{ads}$ is the adsorption energy, $R$ the molar gas constant, and $T$ is the temperature. Adsorbate surface coverage, $\theta$, is defined by the ratio of occupied sites to total number of sites: $C/A_0$, where $A_0$ is the initial (total) concentration of sites. Noting that the equilibrium concentration of sites is $A_0 - C$, the Langmuir equation may be solved for $\theta$:

$$\theta = \frac{KB}{1 + KB} \tag{3}$$

Rowe and Jahanmir and Beltzer utilized this model to define the relationship between wear and additive concentration and between COF and additive concentration, respectively [3,8]. Jahanmir and Beltzer utilized the linear relationship of surface coverage and COF to allow the direct determination of $\theta$ from friction measurements:

$$f = f_b(1 - \theta) + f_a, \quad \theta = \frac{f - f_b}{f_a - f_b} \tag{4}$$

$f$ is the measured COF and $f_a$ and $f_b$ are the coefficients of friction of the additive and base lubricants, respectively. These $\theta$ and the Langmuir model allow the simple determination of $K$ and thus $E_{ads}$ via linear plots of Eq. (5):

$$\frac{1}{\theta} = \frac{1}{K}\frac{1}{B} + 1 \tag{5}$$

Jahanmir and Beltzer also noted the importance of additive lateral (cooperative) interactions effects on adsorption unaccounted for in the Langmuir model. To incorporate such effects those authors utilized a linearized Temkin model, which assumes by its application only repulsive lateral interactions, $\alpha > 0$, and a primary adsorption energy, $E$ [3,9,10]:

$$E_{ads} = E + \alpha\theta \tag{6}$$

A model treating attractive interactions, termed Frumkin–Fowler–Guggenheim (FFG), has also been defined and applied to adsorption data [11]. It has the same fundamental form as the Temkin equation but assumes attractive adsorbate interactions

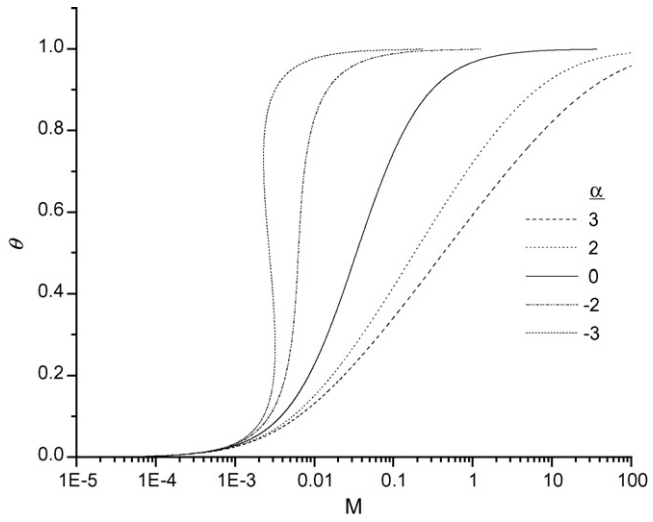


Fig. 1. Example of general adsorption isotherms, arbitrarily $E = -2$ kcal/mol. $\alpha$ is varied from $-3$ to 3 to simulate the dependence of the model on the cooperative interaction parameter.

($\alpha < 0$). As previously noted by Brunauer et al. [10], the Langmuir and the non-linearized Temkin and FFG models are just special cases of the same model if the cooperative interaction term is allowed to be zero, positive, or negative, respectively:

$$K = e^{(-E-\alpha\theta)/RT} \tag{7}$$

This model that does not assume a sign or magnitude of the lateral interaction term, $\alpha$, may be considered a general adsorption model. In Fig. 1, isotherms of this general model demonstrating the effect of $\alpha$ are shown. Unlike the seminal Langmuir model, the general model may not be rearranged to a linear form (e.g. Eq. (5)) without simplifying assumptions [10]. The necessary linearizing assumptions constrain the fitting procedure to independent regions of surface coverage. i.e. $\theta \leq 0.2$, $0.2 \leq \theta \leq 0.8$ and $1 \geq \theta \geq 0.8$ are fit by different equations that are not equivalent to the general adsorption model. Due to its simplicity, the "mid-coverage" equation is utilized almost exclusively for linearized Temkin analyses [10]:

$$\theta = \frac{RT}{\alpha} \ln B - \frac{E}{\alpha} \tag{8}$$

The application of this linearized Temkin model has been demonstrated by Jahanmir and Beltzer and Biresaw et al. [1–3]. The slopes and $y$-intercepts of $\theta$ versus $\ln B$ plots provided the values of $\alpha$ and $E$ and thus the total adsorption energies via Eq. (6) [1–3]. Unfortunately, the focus of previously published studies was the attainment of $E_{ads}$ and the lateral interaction terms were not presented nor discussed [1–3]. The multi-variable fits using the linearized Temkin model will certainly provide improved correlation relative to analogous Langmuir fits. Thus superior correlations of linearized Temkin fits are not necessarily indicative of the model's success. Further, large amplitude changes that occur over relatively small concentration ranges are not readily observable via such analyses. The use of now ubiquitous iterative non-linear fitting computational software allows an absolute examination of the adsorption isotherms independent