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REVIEW ARTICLE

Some consideration triggered by misquotation of Temkin model and the derivation of its correct form

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Abstract Accuracy of quotations is very important for the transmission of scientific knowledge, whereas the misquotations may significantly diminish the academic value of the paper. Recently, Sulyman et al. (2021) published a high academic paper to reveal the adsorption of crystal violet from aqueous solution by a new composite adsorbent in Arabian Journal of Chemistry (2021) 14, 103115. However, the Temkin isotherm was misquoted, which triggered some consideration on the correct form of Temkin model. The present study reviews the original Temkin model proposed by Mikhail I. Temkin in the 1930s, and derives the correct Temkin model by using the adsorption theory. The most striking feature of the Temkin model in its correct form is that the dimensions on both sides are consistent and dimensionless, and the unit of adsorption heat parameter (b_T) is J/mol. Unfortunately, the dimensions of the Temkin model widely cited in the literature are imbalanced, and the unit of b_T is confusing. If there is a quotation error in a published paper, it may mislead readers. This comment can deepen readers' understanding of the Temkin model, avoiding the misuse and propagation of its wrong form.

1. The misquotation of Temkin model

Recently, Sulyman et al. (2021) published a paper entitled "Development, characterization and evaluation of composite adsorbent for the adsorption of crystal violet from aqueous solution: Isotherm, kinetics, and thermodynamic studies" in Arabian Journal of Chemistry (2021) 14, 103115. There is no doubt that it is a highly academic paper. However, the Temkin model cited in their paper is noteworthy. In Section 3.3, Isotherm studies, a linear form of Temkin isotherm is given by the original Eq. (8) which cited from Jain and Gogate's paper (Jain and Gogate, 2018).

$$q_e = \frac{RT}{b_T \ln K_T} + \frac{RT}{b_T \ln C_e} \tag{1}$$

where R (8.314 J mol^{-1} K^{-1}) is the gas constant, T is the absolute temperature (K), b_T is the Temkin constant related to the heat of adsorption (kJ mol^{-1}), K_T is the equilibrium binding constant (L g^{-1}).

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However, we found that this is a quotation error. In the paper of Jain and Gogate (2018), the Temkin model is given as follows:

$$q_e = B_T \ln(K_T C_e) \tag{2}$$

where K_T (L/mg) and B_T (mg/g) are the Temkin model constants.

Obviously, Eqs. (1) and (2) are not the same equation, and both of them are not interchangeable. Further tracing another literature (ALOthman et al., 2013) which Sulyman et al. cited in their paper, the linear form of Temkin isotherm model is described as follows:

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \tag{3}$$

where b_T is the Temkin constant related to the heat of sorption (kJ/mol), K_T is the equilibrium binding constant corresponding to the maximum binding energy (L/g), T is the absolute temperature (K), and R is the gas constant (8.314×10^{-3} kJ/mol K^{-1}).

By comparing Eqs. (2) and (3), B_T should be equal to RT/b_T, which agrees with the previous reports (Klett et al., 2014; Hosseini-Bandegharaei, et al., 2014; Ahmad and Haseeb, 2017; Kankrej et al., 2018; Ahmadi-Pour et al., 2018; Tran et al., 2020). But, strangely, the unit of B_T (mg/g) in Eq. (2) is inconsistent with that of RT/b_T (dimensionless) in Eq. (3). As a result of the above contradiction phenomena, there must have been a mistake in the application of Temkin model. After extensive literature investigation, it is found that Eq. (3) is the popular expression of Temkin model in published papers (Velempini et al., 2019; Zhao et al., 2020; Janu et al., 2020; Zaman et al., 2022; Yusuff et al., 2022; Zhao et al., 2022; Ogbodo et al., 2021). Unfortunately, Eq. (3) is actually a pseudo-equation. The reasons come down to the following three aspects. Firstly, the dimension on both sides of Eq. (3) is imbalanced. In order to verify this problem, the unit of each parameters is substituted into Eq. (3), we have.

$$q_e(mg/g) = \frac{R(J/mol \cdot K) \times T(K)}{b_T(J/mol)} \ln[K_T(L/g) \times C_e(g/L)] = \text{dimensionless} \tag{4}$$

It can be seen from Eq. (4) that the unit on the right-hand side is dimensionless due to the unit offset each other, but the unit on the left-hand side is not dimensionless due to different substances (mg/g, i.e., milligram of adsorbed solute per gram adsorbent). According to the dimensional principle of physics, a correct physical equation must have the same dimension on both sides (Yan, 2012). Since the dimension of Eq. (3) is imbalanced, it is an incorrect equation.

Secondly, Eq. (3) is inconsistent with the original model proposed by Temkin. The Temkin model was firstly proposed by Mikhail I. Temkin (1908–1991), a former Soviet physical chemist in 1930s when he worked with A.N. Frumkin for the hydrogen equilibrium on platinum (Murzin, 2019). And then Temkin and his collaborators published the famous Temkin model when they studied the adsorption behavior of nitrogen on the heterogeneous surface during the ammonia synthesis and decomposition (Boudart, 1993, 1994).

$$\theta = (1/f) ln(a_0 P) \tag{5}$$

where θ is the coverage fraction of nitrogen on the catalyst surface, dimensionless; P is the equilibrium pressure of nitrogen, Pa; a_0 is the adsorption equilibrium constant, Pa^{-1}; f is the coefficient.

Setting $1/f = RT/b_T$, $a_0 = k_T$, $P = P_e$, Eq. (5) can be transformed into:

$$\theta = \frac{RT}{b_T} \ln(k_T P_e) \tag{6}$$

where k_T is the equilibrium constant for gas–solid adsorption, Pa^{-1}; P_e is the equilibrium pressure of gas, Pa. R, T and b_T are the same as those in Eq. (3). Both sides of Eq. (6) are dimensionless, so the original Temkin model conforms to the dimensional principle.

If the Temkin model is also suitable for describing the adsorption behavior of the liquid–solid process, the equilibrium pressure of gas (P_e) and the equilibrium constant (k_T) in Eq. (6) can be replaced by the equilibrium concentration of solute (C_e) and the equilibrium constant (K_T) respectively, yields.

$$\theta = \frac{RT}{b_T} \ln(K_T C_e) \tag{7}$$

where K_T is the equilibrium constant for liquid–solid adsorption, L mg^{-1}; C_e is the equilibrium concentration of solute, mg L^{-1}. Apparently, Eq. (7) also conforms to the dimensional principle. By comparing Eq. (3) and Eq. (7), it can be found that the difference of both equations is on the left-hand side. Although the right-hand side of both equations is identical, the left-hand side of Eq. (3) and Eq. (7) is q_e and θ respectively. Therefore, Eq. (3) is a misquoted equation deviated from the original Temkin model.

Thirdly, some researchers have limited insight into the adsorption heat parameter (b_T) in the Temkin model. For example, in some published literature, the adsorption heat parameter in Temkin model is expressed by b_T with an unit of J/mol (Wibowo et al., 2017; Ma, 2017; El-Maghrabi et al., 2019; Kaur et al., 2019), but in other literatures, the adsorption heat parameter is expressed as $B[B=(RT/b_T)]$ with an unit of J/mol (Zhou et al., 2015; Kankrej et al., 2018; Mamaní et al., 2019; Ghahremani et al., 2021). If the unit of B is J/mol, in this case, the unit of b_T should be dimensionless. The paradox above indicate that some authors lack an understanding of the parameters in the Temkin model.

In order to clearly understand the problem of misuse of the Temkin model and put forward correct solutions, the present study derives the Temkin model by using the adsorption theory. Through this process, readers can deepen their understanding of the Temkin model, and then accurately answers the following two questions: (1) the correct form of Temkin model; (2) the physical meaning of each parameter in the Temkin model.

2. Theoretical derivation of the Temkin model

Although the Temkin model takes into account the heat of adsorption and the interaction between the adsorbent and adsorbate (Foo and Hameed, 2010; Ma et al., 2016; Ahmadi-Pour et al., 2018), it also can be derived by theoretical method (Yang, 1989). According to the molecular collision theory and

the assumption of monolayer adsorption, the adsorption rate of gas molecules on the solid surface is proportional to the gas pressure and the vacant ratio of active adsorption sites on the solid surface, and inversely proportional to the adsorption activation energy of gas molecules, so the adsorption rate r_a can be expressed as (Atkins, 1978; Fu et al., 2005):

$$r_a = k_a P(1-\theta)e^{\frac{-E_a}{RT}} \tag{8}$$

where r_a is the adsorption rate of gas molecules, s^{-1}; P is the gas pressure in the adsorption system, Pa; k_a is the adsorption rate constant, Pa^{-1} s^{-1}; θ is the coverage fraction of gas on the adsorbent surface, dimensionless; (1-θ) is the vacant ratio of active adsorption sites on the adsorbent surface, dimensionless; E_a is the activation energy for adsorption of gas molecules, J mol^{-1}. R is the gas constant, 8.314 J mol^{-1} K^{-1}; T is the absolute temperature, K.

The desorption rate of gas molecules adsorbed on the solid surface is proportional to the coverage ratio θ and inversely proportional to the desorption activation energy of gas molecules, i.e.

$$r_d = k_d \theta e^{\frac{-E_d}{RT}} \tag{9}$$

where r_d is the desorption rate of gas molecules, s^{-1}; k_d is the adsorption rate constant, s^{-1}. E_d is the activation energy of desorption, J/mol;; The adsorption equilibrium constant $K = k_a/k_d$, so the unit of K is Pa^{-1}.

In the ideal adsorption layer, the active sites on the solid surface are evenly distributed, and the energy of each active center is the same, so the activation energy of adsorption and desorption does not change. However, as far as the adsorption of real gas on heterogenous surface is concerned, the activation energy of adsorption and desorption are no longer constant. If the adsorption process conforms to the Temkin model, the adsorption activation energy increases linearly with θ, while the desorption activation energy decreases linearly with θ (Aluigi et al., 2014; Ahmadi-Pour et al., 2018; Fu et al., 2005), i.e.

$$E_a = E_a^o + \beta\theta \tag{10}$$

$$E_d = E_d^o - \gamma\theta \tag{11}$$

where E_a^o is the initial activation energy of adsorption, J/mol; β is the coefficient of adsorption activation energy increasing with the increase of adsorption fraction coverage, J/mol. E_d^o is the initial activation energy of desorption, J/mol; γ is the coefficient of desorption activation energy increasing with the increase of adsorption fraction coverage, J/mol. Both β and γ are parameters related to activation energy. Understanding the unit and meaning of these two parameters is helpful to correctly understand the adsorption heat parameter b_T.

Substituting Eqs. (10) and (11) into Eqs. (8) and (9) respectively, we have,

$$r_a = k_a P(1-\theta)e^{\frac{-E_a^o}{RT}}e^{\frac{-\beta\theta}{RT}} \tag{12}$$

$$r_d = k_d \theta e^{\frac{-E_d^o}{RT}}e^{\frac{\gamma\theta}{RT}} \tag{13}$$

Since E_a^o and E_d^o remains constant during the adsorption process, the terms of exp(-E_a^o/RT) and exp(-E_d^o/RT) can be incorporated into the rate constant of k_a and k_d, respectively. In addition, since θ varies between 0 and 1, the effects of (1-θ) and θ on the adsorption and desorption is far less than those of activation energy when the value of θ is low (Fu et al., 2005). Therefore, the terms of (1-θ) and θ can also be incorporated into the rate constant of k_a and k_d respectively. Through such simplification, Eqs. (12) and (13) can be transformed into.

$$r_a = k_a' P e^{\frac{-\beta\theta}{RT}} \tag{14}$$

$$r_d = k_d' e^{\frac{\gamma\theta}{RT}} \tag{15}$$

At equilibrium, the adsorption rate r_a equals the desorption rate r_d, and $P = P_e$, i.e.:

$$k_a' P_e e^{-\frac{\beta\theta}{RT}} = k_d' e^{\frac{\gamma\theta}{RT}} \tag{16}$$

Rearranging Eq. (16) and setting $b_T = \beta + \gamma$, $K_G = k'_a/k'_d$, yields.

$$K_G P_e = e^{\frac{b_T}{RT}\theta} \tag{17}$$

Taking the logarithm of Eq. (17) gives:

$$\theta = \frac{RT}{b_T}\ln(K_G P_e) \tag{18}$$

where b_T is the adsorption heat parameter and its unit is the same as β and γ, J/mol; K_G is the adsorption equilibrium constant of gas molecules on the solid surface, Pa^{-1}; P_e is the gas equilibrium pressure, Pa.

Eq. (18) is the correct Temkin model describing gas-solid adsorption. The left-hand side of Eq. (18) is the term of θ which is dimensionless, and the right-hand side of Eq. (18) is the term of $[(RT/b_T)\ln(K_G P_e)]$ which is also dimensionless. If $RT/b_T = 1/f$, $a_0 = K_G$, $P_e = P$, then Eq. (18) reverts to Temkin's original model (Eq. (5)), indicating that both of them is identical.

However, the parameter θ is not easy to measure, leading to the difficulties of Eq. (18) in application. In order to solve this problem, the parameter θ can be replaced by the ratio of the equilibrium adsorption amount (q_e) to the saturated adsorption amount (q_m) (Yang, 1998; Otake et al., 2004):

$$\theta = \frac{q_e}{q_m} \tag{19}$$

Substituting Eq. (19) into Eq. (18), yields,

$$\frac{q_e}{q_m} = \frac{RT}{b_T}\ln(K_G P_e) \tag{20}$$

Eq. (20) is another form of Eq. (18), and both of them are equivalent. Using the same principle, the Temkin model for liquid–solid adsorption can be derived as follows:

$$\frac{q_e}{q_m} = \frac{RT}{b_T}\ln(K_L C_e) \tag{21}$$

where q_e and q_m are the equilibrium and saturated adsorption amount of solute on solid surface respectively, mg/g; b_T is the adsorption heat parameter, J/mol; K_L is the adsorption equilibrium constant of solute on solid surface, L/mg. C_e is the equilibrium concentration of the solute, mg/L.

Eq. (21) is the revised form of Eq. (3), which agrees with the original Temkin model and has no the dimensional problem. Up to now, the misquotation of Temkin model is very common. To our knowledge, only a few authors used the correct form of Temkin model in their paper (Millar et al., 2015; Li et al., 2015).

3. Conclusions

Although the Temkin equation has been widely used in the adsorption field, the problem of dimensional imbalance has been ignored, and the quotation errors are very common in the literature. This paper reviews the original Temkin model proposed by Mikhail I. Temkin in the 1930s, and derives the correct Temkin equation by using adsorption theory. The most striking feature of Temkin model in correct form is that the dimensions on both sides are consistent and dimensionless, and the unit of adsorption heat parameter (b_T) is J/mol. Unfortunately, the dimensions of the Temkin model widely cited in the literature are imbalanced, and the unit of b_T is confusing. Because readers generally like to read the latest published literature, the misquotation of the Temkin model must be corrected in time. This comment can deepen readers' understanding of the Temkin model, avoiding the misuse and propagation of its wrong form.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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